





# CHEMICAL ABSTRACTS

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## 1—APPARATUS

C. G. DERICK

**Notes on laboratory apparatus.** A. B. ANDREWS. Lewiston. *J. Ind. Eng. Chem.* **13**, 560(1921).—A description of 2 pieces of app., (1) a large capacity autoclave improvised from a 150-cc. shrapnel case, which works automatically for days with a variation of only 2 lbs. at 600–800 lbs. pressure per sq. in., and (2) Au cylindrical cathodes in place of Pt ones for electrolytic Cu detns. C. C. DAVIS

**The "Union" gas calorimeter.** W. FRITSCH. *Brennstoff Chem.* **2**, 155–7(1921).—Description of a gas calorimeter made by the Union-apparatebaugesellschaft, Karlsruhe, for the purpose of measuring the heat of combustion of small quantities of gas—ranging from 4–6 cc. in the case of  $C_2H_2$  to 50–60 cc. in the case of mine gases. The combustion buret is surrounded by a jacket containing "petroleum oil," which on expanding owing to the heat of combustion, rises in the capillary side-arm, graduated in mm. The app. is calibrated by the combustion of a known vol. of H-O mixt., which is evolved from Pt electrodes in the buret itself. Sources of error have been studied by the Gasinstitut, Karlsruhe, and by the Kaiser Wilhelm Institut für Kohlenforschung, with the conclusion that in general the errors do not amount to more than  $\approx 1.2\%$ , although in some cases they are as high as 4.9%. W. B. V.

**Water heater for analytical work.** S. I. MEYERS. Victorville, California. *J. Ind. Eng. Chem.* **13**, 563(1921).—A heater for supplying  $H_2O$  at constant temp. consists of a closed and insulated cylinder heated by resistance wires. The  $H_2O$  spout is also heated by wire windings in series with a lamp or hot plate to prevent injury to the rubber tubing. The cylinder is maintained full by a siphon from a  $H_2O$  reservoir. C. C. DAVIS

**Apparatus for the rapid determination of the available chlorine in bleach liquor.** MORRIS SCHERO. Holyoke. *J. Ind. Eng. Chem.* **13**, 559–60(1921).—Hydrometer detn. of bleach liquor for available Cl is unreliable, and titration methods are not adaptable to the ordinary paper-mill personnel. App. has been devised for use by inexperienced men; it is suitable also for permanganates, peroxides, perborates and carbonates. Essentially it measures the pressure of O from the action of  $H_2O_2$  on a hypochlorite. It is claimed to fall within 0.02 lb. of Cl per gal. of 35% bleach liquor of the results of  $Na_2S_2O_4$  titrations. Two bulbs are connected by a stopcock and a by-pass. The upper bulb connects with a manometer with sliding scale. Directions for constructing the scale and calibrating the app. are given. A detn. consists merely in filling the lower bulb through an opening with bleach liquor, the upper bulb with  $H_2O_2$ , closing the lower bulb, opening the stopcock, reading the pressure and applying the formula for the particular instrument. Temp. variations are disregarded. C. C. DAVIS

**Direct-heat rotary drying apparatus.** R. G. MERZ. *J. Ind. Eng. Chem.* **13**, 449–52(1921).—This class of drying app. which was originated to handle large quantities of minerals, consists of a furnace for combustion of fuel, a horizontally mounted revolving steel shell, and a discharge chamber. The passage of gases and materials is through the steel shell. M. discusses various types as single shell, compartment, cellular, double shell, tubular (as regards construction); and as direct, semidirect and



indirect as regards application of heat. There is little to justify counter-current operation. Industrial applications are discussed. The advantages are large capacity, high efficiency, simplicity, ease of inspection, low maintenance and freedom from shutdowns. The possible disadvantages are dust losses, overheating of material, production of unpleasant odors and dust or gas explosions. The factors which affect the thermal efficiency are discussed.

C. C. HERITAGE

**Tunnel dryers.** G. B. RIOLEY. *J. Ind. Eng. Chem.* **13**, 453-80(1920).—The type of dryer discussed consists of a tunnel supplied with heated air, through which the material passes on trays. The air can be heated by steam coils, a hot-air furnace or direct heat can be employed. The heated air is conveyed by fans, either suction or pressure being used. Charts and nomographs are given for the detn. of headway, tunnel car hrs., wet capacity in lb. per hr. per sq. foot tray area, total wet capacity in tons per 24 hrs., etc. The so-called wet dry ratio is discussed. A typical calcn. of the amt. of air required is made. The relation of vapor pressures to rate of evapn., the optimum air velocity, usual limits being 300 and 1000 feet per min., the factors governing drying temp., direction of passage of material with respect to heated air and recirculation of air as a humidity control are discussed. Thermal furnace efficiencies above 90% are obtained with direct heating, burning fuel oil. The operation of a *fruit-dehydrating plant* is described.

C. C. HERITAGE

**The automatic electric bake oven.** JOHN M. STRAIT AND J. C. WOODSON. *Elec. J.* **18**, 296-300(1921).—Detailed illus. account.

C. G. F.

**The limits of measurement by means of refractometers.** H. SCHULZ. Opt. Instit. C. P. Goertz A. G. Berlin Friedenau. *Chem. Umschau* **28**, 138-41(1921).—Illust. An ideal universal refractometer for solids and liquids should range from 1.3 to 2.0, but the glass prisms in use require such high Pb content for the upper limits that the glass becomes too soft and non-resisting to wear, and 1.68 is the practical upper limit. The accuracy of instruments of large range is not as great as of those of shorter range. A new universal instrument is described and illustd., made by C. P. Goertz, Berlin, for aq. and alc. solns. for different temps., with 2 scales, ranging from 1.30 to 1.53.

P. ESCHER

**Viscosimeter with temperature regulation.** W. R. HESS. *Arch. ges. Physiol.* **180**, 61-7(1920).—The significance of changes in viscosity, from the theoretical as well as from the practical point of view, particularly in clinical medicine is dependent upon accuracy of detn. Variable temp. may introduce a considerable error, and to avoid this the app. of the author has been provided with a water jacket. Details of construction and operation are given.

G. H. S.

**Instruments based on the temperature variation of resistance.** Resistance thermometry, etc. Platinum thermometers, a compensated bridge, a compensated bolometer, and the radio-balance. II L. CALLENDAR. *Proc. Phys. Soc. (London)* **33**, 135-8(1921).—(1) A very sensitive Pt thermometer made by Lea and Craskell in 1887 was exhibited. It was one of a differential pair and consisted of 8 ohms of 1 mil pure Pt wire wound on a very thin plate of mica 3 mm. square and insulated with thin plates of mica attached on either side with a special cement. (Brit. pat. 14509, 1887.) (2) Compound thermometers for linear scale. Mention is made of the combination of two suitable metals to make a compl. resistance thermometer giving a linear scale of temp. over a much longer range than a single metal would give. (*Phil. Trans. A*, 1887.) C. points out that this device has since proved useful in special cases, but for accurate thermometry it is better to use a single pure metal and reduce the readings to the gas scale by the difference formula. (3) Compensated resistance box. The Pt-Ag resistance coils are compensated for changes in room temp. by means of a series of Pt compensation coils in the opposite arm of the bridge. Each pair of coils was separately adjusted



to a const. difference over the range  $10^{\circ}$  to  $30^{\circ}$  before being placed in the box. Such a box made in 1893 was exhibited. (4) Compensation of thermometers for conduction along leads. A compensated Pt thermometer used at McGill College in 1895 for observing rapid variations of temp. in the cylinder of a steam-engine in detg. the adiabatic index of dry steam, and investigating the phenomena of supersaturation, was exhibited. It consisted of two loops, of unequal length, of 1 mil pure Pt wire welded to two pairs of thick leads of Pt projecting from a glass stem in the end of which they were sealed. The fine wires followed the variations of temp. of the steam with almost incredible quickness. The two loops were connected on opposite sides of the bridge wire so that the observation of the balance-point gave the difference of resistance corresponding to the central portion of the longer loop, automatically cor. for end-effects due to the conduction along the thick leads. The temp. at any point of the cycle was observed by setting a periodic contact to close the circuit of the galvanometer at the desired point. The same method of compensation for end effects has been employed for many similar purposes. (*Proc. R. I.* 1899.) (5) Compensated bolometer. An important application of the same principle was made in the construction of a bolometer for the abs. measurement of radiation by Kurlbaum's method. Two similar grids of different lengths were used differentially as described and exhibited at the meeting of the Physical Society in May, 1905. (6) The radio-balance. The defects of the bolometric method for the abs. measurement of radiation are: (1) non-simultaneity of the elec. compensation, requiring successive observations; (2) uncertainty and difficulty of detn. of the absorption coeff. of the grid. In the radio-balance these objections are met (1) by simultaneous compensation of the radiation by absorption, due to the Peltier effect; (2) by using a cup to receive the radiation admitted through a small circular aperture in such a way that the absorption is practically complete. Several types of radio-balance were exhibited.

C. C. VAN VOORHIS

**Instruments based on temperature variation of resistance. Resistance thermometry, etc.** Early work on the resistance pyrometer. C. R. DARLING. *Proc. Phys. Soc. (London)* **33**, 138-9 (1921).—Brief reference is made to the early work of Sir William Siemens, who was the first to measure temps. by the resistance method; he constructed a copper wire resistance thermometer in 1860. The development of the Pt thermometer is then traced. The three forms of indicating app. that have been used are: (1) A differential voltmeter, in which the resistance of the pyrometer coil was deduced from the vols. of gas liberated in two tubes containing dil. H<sub>2</sub>SO<sub>4</sub>, and each forming part of a differential circuit; (2) an ordinary differential galvanometer circuit in which the pyrometer coil was balanced against an adjustable resistance; and (3) the present Wheatstone bridge arrangement.

C. C. VAN VOORHIS

**Instruments based on temperature variation of resistance. Resistance thermometry, etc.** Resistance thermometers for steam temperatures. C. JAKEMAN. *Proc. Phys. Soc. (London)* **33**, 140-1 (1921).—The construction and operation of a small Pt resistance thermometer with small time lag, for use in steam pipes, are both described in detail.

C. C. VAN VOORHIS

**Instruments based on temperature variation of resistance. Resistance thermometry, etc.** An electric transmitting radiator thermometer. E. A. GRIFFITHS. *Proc. Phys. Soc. (London)* **33**, 141-4 (1921).—An instrument making use of the resistance thermometer to measure the temp. of the water in the engine radiators of an aeroplane is described with the aid of two figures.

C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. The hot-wire microphone.** Experiments illustrating the function of convection currents in determining the sensitivity of the hot wire microphone. W. S. TUCKER. *Proc. Phys. Soc. (London)* **33**, 144-8 (1921).—The hot-wire grid in the diaphragm is protected from drafts by having



a closed cavity at the rear side of the diaphragm and the sound is considerably magnified by having this cavity and the diaphragm aperture constitute a suitable Helmholtz resonator. The effect of convection currents on the sensitivity of the hot wire for responding to oscillatory air currents is illustrated by a study of the "characteristic curve" of a hot wire.

C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. The directional hot-wire anemometer.** J. S. G. THOMAS. *Proc. Phys. Soc. (London)* 33, 149-51 (1921).—The laws of convection of heat from fine heated wires are such as to indicate the hot-wire type of anemometer as more especially the kind of instrument for the precise measurement of the velocity of a slowly moving fluid. The effect of the free convection current in the region of low impressed velocities in the Morris type of hot-wire anemometer is shown by a set of curves. These curves were detd. for both upward and downward flows of the impressed air stream and in each case with the shielded and unshielded wires respectively leading. The author has devised a directional type instrument in which the difficulties originating in the free convection current have been almost entirely eliminated. A bibliography of the author's papers on such an instrument is given.

C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. An instrument for use in measuring convected heat.** A. H. DAVIS. *Proc. Phys. Soc. (London)* 33, 152-63 (1921).—If air, of density  $\rho$  and temp.  $\theta$  flowing with velocity  $v$ , was originally at  $0^\circ$ , then the air has been supplied with heat which is passing a section normal to the stream at the rate of  $v\rho s\theta$  Cals. per sq. cm. per sec.,  $s$  being the known specific heat at const. pressure. A special type of hot-wire anemometer is used to measure  $v\rho$ , independently of the temp. of the air, and adapted for use as a resistance thermometer to obtain  $\theta$ . The instrument is constructed in two types, one being a null instrument and the other being direct reading, and thus more convenient but involving an approximation which somewhat restricts its range. Full descriptions of the construction and operation of both types are given.

C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. The katharometer.** G. A. SHAKESPEAR. *Proc. Phys. Soc. (London)* 33, 163-4 (1921); cf. C. A. 15, 2.—A brief description is given of the construction and operation of both the single-flow and the double-flow katharometer. The sensitiveness of the katharometer is remarkable, as 1 p.p.m. of H in air could be detected. During the war it was used in the measurement of the permeability of balloon fabrics to H and other gases; the detection of leakages in balloons, the improvement of the seams where the fabric joined; and the detection of H in air and of air in H. The author has used the instrument in conjunction with a "thread recorder" as a recording hydrometer for continuous records of humidity for many months. The double-flow form of instrument is extremely useful for measuring small traces of impurity in certain cases. Various communications on the subject by Shakespear and Daynes will be found in the Reports of the Advisory Committee on Aeronautics 1916-18.

C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. Industrial applications of the katharometer.** H. A. DAYNES. *Proc. Phys. Soc. (London)* 33, 165-9 (1921); cf. C. A. 15, 2 and preceding abstract. The points in favor of the use of this method of analysis in controlling manufg. processes are: (1) it gives a continuous reading, making intermittent withdrawals and analyses of gas samples unnecessary; (2) the reading of the instrument is independent of the rate of gas flow through it; (3) the instrument is very quick in action; (4) the zero of the instrument is reasonably independent of variation of temp. and (5) of the current through the bridge; (6) the thermal cond., on which the operation of the instrument depends, is very nearly independent of atm. pressure; (7) the instrument can be made robust; and (8) calibration and standardiza-



tion are easy, parts can be made completely interchangeable and any number of elements can be connected to a single recorder or indicator. The disadvantages are: (1) it can give no qualitative analysis, and quantitative ones only in certain special cases; (2) the sensitiveness depends slightly on temp; and (3) the sensitiveness depends very largely on the current in the bridge, being nearly proportional to the cube of the current. The chief field for the method is in the cases of binary mixts. of known constituents. Applications in addition to those in the preceding abstracts are: the measurement of H and N in mixts. during the synthesis of  $\text{NH}_3$ , and detns. of the amts. of  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  in air. The special precautions necessary in the use of this method for the analysis of certain complex gas mixts. such as detn. of  $\text{CO}_2$  in flue gases or  $\text{H}_2\text{O}$  in furnace gases are given. Also there is a short bibliography attached. C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. The calometer.** L. HILL AND (Miss) HARGOOD-ASH. *Proc. Phys. Soc. (London)* 33, 169-71 (1921).—The calometer is an instrument which measures the heat loss of a wire coil maintained at a const. temp. The coil, which is made of a resistance wire having a large coeff. of resistance, is made one arm of a Wheatstone bridge. By a suitable arrangement the current through the coil is automatically regulated so as to keep the coil temp. at  $34^\circ$  (body temp.). An ammeter in series with the coil shows the amt. of current required to maintain the const. temp., thus making possible the calcn. of the heat loss under varying conditions of the gas surrounding the coil. The instrument may be made self-recording. Thus the calometer enables the meteorologist or hygienist to record daily variations of the rate of cooling of a surface at body temp. produced by atm. conditions. Records taken out-of-doors throw light on the conditions which lead one to define the weather as pleasant, unpleasant, bracing, muggy, etc. Records taken indoors are a valuable guide in securing adequate ventilation. To make a recording katalometer the calometer coil is placed within the bulb. C. C. VAN VOORHIS

**Instruments based on temperature variations of resistance. Liquid depth gage, distant reading type.** E. A. GRIFFITHS. *Proc. Phys. Soc. (London)* 33, 171-3 (1921).—A thin Pt wire is elec. heated to about  $20^\circ$  above the surrounding air. The wire is insulated and suitably protected by a tube open at the bottom and near the top, projecting the full depth of the tank. This wire is made one arm of a Wheatstone bridge, while in another arm is placed a similar wire located alongside the first but totally sealed off from the liquid, thus making it possible to eliminate the effects of temp. changes of the liquid and the atm. above it. The change of the resistance of the partially immersed wire with variations of liquid level is indicated by the deflection of the galvanometer pointer. The current through the bridge must be kept const.; this can be accomplished in several ways, most of which are too complicated to be of service on airplanes where the device was used to gage the depth of gasoline in the tanks. Here a ballast resistance of iron wire in H was found to be very serviceable; it maintains a fairly const. current with voltage changes up to 20%, thus making frequent adjustment of the current unnecessary. C. C. VAN VOORHIS

**An improved form of Reichsauer's pycnometer.** R. SAAR. *Chem.-Ztg.* 45, 102-4 (1921).—If the actual wt. of  $\text{H}_2\text{O}$  which a pycnometer is found to contain be subtracted from the wt. which it is supposed to contain and this difference subtracted from the wt. of the empty app., the result is an "apparent tare wt." for that particular app. To get the sp. gr. of any liquid it is only necessary to subtract this "apparent tare wt." from the wt. of the app. filled with the liquid and multiply the remainder by 0.02 for a 50-cc. pycnometer, or by 0.01 for a 100-cc. app. This rapid method has been applied to the improved app. in the form of 2 scales on the stem from which corrections are read, thus obviating much of the trouble experienced in using the ordinary app. Examples in using the app. are given. J. H. MOORE



**A revolving burner.** GEORG LOCKEMANN. Robert Koch Inst., Berlin. *Z. angew. Chem.* **34**, Aufsatzteil, 198(1921); 1 cut.—The app. is designed to heat all sides of a crucible or dish. A wheel is mounted in a horizontal position on 1 end of a horizontal shaft clamped to a lab. stand. The base of the burner works in a bearing on the inner end of a bent arm reaching to the center of the wheel, the outer end of the arm being attached to the upper side of the rim of the wheel by means of a clamp screw, so that the burner may be placed out of line with the axis of the wheel as much as the size of the dish to be heated may require. When the wheel revolves the burner describes a circle under the dish. There are 2 grooves in the face of the wheel, 1 for the belt from a motor and the other for a belt to drive a 2nd burner, etc., several of which may be driven by 1 motor. Cf. *C. A.* **14**, 2106. J. H. MOORE

**Rheostat which occupies very small space.** ANON. *Elec. World* **78**, 28(1921); 1 illus.—The resistor consists of a metal ribbon. One of the rheostats designed for 3 kw. continuous duty occupies a space of 25 cm.  $\times$  25 cm.  $\times$  30 cm. and weighs 3.7 kg. An equally compact 9 kw. unit weighs 37 kg. Full details are given. C. G. F.

**Resistors for use with various types of controllers.** C. J. KIRKASSER AND E. W. SEEGER. *Elec. Rev.* **79**, 123-8(1921); 14 illus.—A detailed description of the various materials entering into the construction of rheostats; the importance of ample ventilation for continuous service units, etc. Many lab. types are shown. C. G. F.

**The "invisible" wet air filter.** ANON. *Electrician* **86**, 799-801(1921).—This filter washes the air, removes all dust and solid matter, and delivers the air to the generator clean, humid, and at a much lower temp. than the atm. The air is cleansed by passing it into the base of the machine, through openings fitted with steel covers. Upper surfaces are constructed of expanded metal. The air passes through a large number of thin galvanized steel plates, which stand vertical and are arranged to make a complete circle. The plates are bent into the form of a true involute, enabling them to be equidistant at all points. Small projections pushed out of the plates themselves keep them in position. The plates are kept wet by slowly revolving spray arms. The action is like that of a fish's gill. Each cu. ft. of air comes in contact with 200 sq. ft. of filtering surface. From the filter unit the air is drawn over a system of vertical eliminator plates which prevent free moisture passing over into the ducting and remove stray dirt particles. The machine consists of a circular cast Fe tank in the center of which is placed a vertical hollow bronze spindle. Mechanical features are described in detail. A practical efficiency test consists of drawing a known quantity of air through a small filter composed of a single sheet of white blotting paper clamped to leave a small circle of 0.5 cm. diam. The air passes through this exposed disc section and if the air is not properly cleansed a black disc will result. W. H. BOYNTON

**The thermal effect produced by a slow current of air flowing past a series of fine beated platinum wires, and its application to the construction of hot-wire anemometers of great sensitivity, especially applicable to the investigation of slow rates of flow of gases.** J. S. G. THOMAS. So. Metrop. Gas. Co., London. *Phil. Mag.* [6] **40**, 240-50(1921); cf. *C. A.* **14**, 2280. Further work giving calibration curves using a new flow tube constructed on the same principle as already described. S. C. LADD

**The economy of the so-called automatic return-feed apparatus in steam boiler plants.** HUBERT KRANTZ. Aix la Chapelle. *Chem. App.* **8**, 104-6(1921).—Birk's conclusion (*C. A.* **15**, 1173) that feed-pumps are more economical than the automatic system is based on erroneous assumptions and errors in calcn., and claims that the automatic feed costs only  $\frac{1}{4}$  to  $\frac{1}{10}$  as much to operate as pumps. J. H. MOORE

**The usefulness of condensate traps in distillation plants.** W. HUEBELING. *Chem. App.* **8**, 96-7(1921); 1 cut.—H. agrees with Birk's statement (*C. A.* **15**, 1834) that



the condensate pump is the only reliable app. for this purpose and claims that the float trap "Missong," made by Bopp & Reuther, Mannheim-Waldhof, is reliable.

J. H. MOORE

#### Thermoelements (PFLEIDERER) 2.

**Thermocouple for high-temperature measurement.** T. TAKIZAWA, J. TSUKAMOTO and TOKYO DENKI Co. Japan 36,602. June 15, 1920. A couple is made of W and Mo wires, enclosed in a porcelain tube, which is maintained in vacuum or filled with H or A, preferably H at  $2/3$  atm. It is used for the interval 1,500–1,850°. The e. m. f. of this couple increases proportionately to the increase of temp. at low-temp. interval; thermoelectric inversion occurs at 530°; the e. m. f. decreases, reaching zero near 1,300° and changes direction. The e. m. f. in mv. is as follows: 1500° 2.82, 1600° 3.49, 1700° 4.25, 1800° 5.20, 1900° 6.20.

## 2—GENERAL AND PHYSICAL CHEMISTRY

WILLIAM E. HENDERSON AND EDWARD MACK

**The work of Dr. Blas Cabrera.** HORACIO DAMIANOVICH. *Anales soc. quim. Argentina* 8, 277–82(1920).—A biographical sketch. L. E. GILSON

**The history of chemistry.** JOHN JOHNSTON. *Sci. Monthly* 13, 3–23, 130–43 (1921). E. H.

**The university and research.** VERNON KELLOG. *Science* 54, 19–23(1921). E. H.

**How must chemical instruction in the higher schools be revised and what can industry and technics afford in this?** P. STAUTZ. *Chem.-Ztg.* 45, 493–4(1921). E. H.

**Chemical nomenclature and pronunciation.** J. NORMAN TAYLOR. *J. Am. Pharm. Assoc.* 10, 10–11(1921).—A plea for the use of the final letter in the spelling of many chemical terms. T. objects to the shortened form of such words as "chlorine" and "sulfate." L. E. WARREN

**Synthetic helium and neon.** A. LO SURDO. *Atti r. accad. Lincei* [v] 30, 1, 85–8 (1921).—L. finds that Ne, He, and H are able to pass through hot glass, the H in far greater quantity than the other two gases. The passage is dependent on the temp., nature, and thickness of the glass. These results may furnish an explanation for the origin of so-called synthetic He and Ne, which may be derived from the atm. J. C. S.

**Asymmetry of gas molecules.** A contribution to the determination of molecular form. RICHARD GANS. *Ann. Physik* 65, 97–123(1921).—This paper comprises largely a re-investigation of the whole subject of *Tyndall effects* in gases, already intensively studied by Strutt, whose original papers are to be found in *Proc. Roy. Soc. London* (A) 94, 453; 95, 155(1918). The method and app. are those of Strutt with important refinements such as the use of parallel light. These are described in detail. Of particular importance is the measurement of the transparency of the filter placed before the photographic plate in the app. This filter, itself a photographic plate with the gelatin scratched from the upper half, enables the weak horizontally vibrating rays of light to pass only through glass while the strong vertical rays must also pass through the black Ag layer of the absorption screen. The method of measuring consisted in so selecting the filter that the blackening of both images upon the plate appeared equal. Knowing the transparency of the filter the degree of polarization may be at once detd. The transparency is detd. from the relation  $T = (d_1/d_2)^2$ , where  $d_1$  and  $d_2$  are the thicknesses of 2 screens made by cutting a convergent lens so that the rays from one pass through the clear glass and those from the other pass through the black layer of the absorption



filter and give 2 images upon the photographic plate of equal intensity. Using the formulas of Langevin developed from the electromagnetic theory (cf. *Le radium* 7, 249(1910)) the asymmetry of the mol. and the Kerr effect are considered. Dimensions are calcd. from the Clausius-Mossott theory of mol. form and agree both with those of Strutt and those calcd. from the kinetic theory. The elliptical cross sections of He, CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S are diagrammatically represented. While the depolarization of the Tyndall light and the Kerr phenomena in gases can be explained only by the asymmetry of mols. there is also in isotropic combinations of the vibrating particles a magnetic rotation of the polarization planes. Finally an effort is made to discover to what extent the constants developed can also explain the Faraday effect. The mathematical treatment gives very good agreement for  $\rho$  calcd. from magnetic rotation and from circular polarization.

G. L. CLARK

The coagulation of colloidal arsenic sulfide. Principle of a method of study. A. BOUTARIC AND M. VUILLAUME. *Compt. rend.* 172, 1293-6(1921).—The method consists in measuring with a spectrophotometer the rate of change in the opacity of the arsenious sulfide sol resulting from the addition of a soln. of an electrolyte. 50 cc. of the sol are dild. with 50 cc. of water and the opacity,  $x_0$ , is measured, using the spectral region  $\lambda = 575 \text{ m}\mu$ . Then 50 cc. of the sol are mixed with 50 cc. of the electrolyte soln. and the opacity,  $x$ , is measured at time  $t$ . Plotting  $x - x_0$  against  $t$  gives a curve rising at first rapidly, then more slowly, finally attaining a max. At this max. coagulation results if the sol is disturbed slightly as by agitation or by tobacco smoke, the behavior resembling that of a supersatd. soln. (The fact that the sol if undisturbed may not coagulate for some time indicates a possible source of error in previous expts. in which the time required for a given electrolyte soln. to cause coagulation is measured.) The presence of an excess of H<sub>2</sub>S or of As<sub>2</sub>O<sub>3</sub> in the sol alters the rate at which the max. of the curve is attained.

F. L. BROWNE

A cause of the dispersion of the colloid in an important class of hydrosols. A. TIAN. *Compt. rend.* 172, 1291-3(1921).—Solns. of salts whose base (or acid) is sparingly sol. are hydrolyzed, yielding hydrosols of the base (or acid). Within wide limits such hydrosols are reversible. This is the result of a chem. reaction taking place at the interface between the particles of the hydrogel and the aq. phase. At the surface the hydrolysis is forced back, forming the salt, which diffuses away into the aq. phase. Here it again hydrolyzes, forming particles of the base much smaller than the original particles. This process continues, giving continually smaller particles until the hydrosol is formed. The peptization of heavy metal hydroxides by their salts, e.g. Fe(OH)<sub>3</sub> by FeCl<sub>3</sub>, is accounted for in this way. The detergent action of soaps is an important com. application.

F. L. BROWNE

The ultramicroscopic study of manganous arsenate jellies. FR. FLADÉ, H. SCHERFFIG, AND E. DEISS. *Z. anorg. allgem. Chem.* 116, 228-30(1921).—Photomicrographs are shown of the manganous arsenate jellies made by mixing manganous chloride and potassium arsenate solns. (*C. A.* 8, 2658.) The jellies are characterized by a fibrous structure. On standing they gradually break down, leaving a ppt. consisting of leaf- or plate-shaped crystals. The existence of the jelly is possible only as long as the dispersed phase retains a fibrous structure.

F. L. BROWNE

The soaps as protective colloids for colloidal gold. THOMAS IREDALE. *J. Chem. Soc.* 119, 625-34(1921).—Gold chloride was reduced by hydrazine hydrate in the presence of the Na salts of cerotic, nonic, lauric, palmitic, stearic and oleic acids present in varying percentages. In most cases there is a max. soap concn. for optimum results; beyond this the concn. of Na ions probably negatives the protective action of the soap. Na oleate and stearate were most efficient, while Na nonoate had almost no protective action. Practically dry colloids could not be made containing over about 10% Au.



which indicates that soaps are inferior to such protectors as Na lysalbate. The originally ruby-red sols containing soap are changed to blue by the addition of acid; NaCl, or alcohol. In alcoholic soln. the soaps are crystalloidally dissolved and do not act as protectors. The fact that Na oleate and stearate have pronounced protective action even at a concn. of 0.001% militates against McBain's view that at great dilns. both dissociated and undissociated soaps are crystalloids of simple mol. wt., for the expts. with alcohol show that soaps in truly mol. condition are not adsorbed by gold.

JEROME ALEXANDER

The determination of the sorption of both solvent and solute. I. The system: benzene-iodine-charcoal. ABU MOHAMED BAKR AND JOSEPH EGDAR KING. *J. Chem. Soc.* 119, 454-60(1921).—A general method is described of detg. the true amts. of sorption of both solute and solvent, to supplement the ordinary method, which yields relative values only. It consists in exposing C to the vapor of the soln. and likewise to that of the pure constituents, so that equil. is attained through the vapor phase. The objection with regard to condensation of liquid in the capillaries and pores of the sorbing agent is obviated by keeping the latter at a temp. far above that of the liquid with the vapors of which it is in equil. As a matter of fact, however, the error in the ordinary method, consisting in shaking a certain vol. of soln. of known strength with a known amt. of sorbing material and analyzing a sample of the remaining soln., is inappreciable except in concd. soln. or where the solute does not exhibit strong positive sorption. In such cases both the proportionality factor and the exponent in the exponential formula are altered. Sorption of benzene from 1 solns. is less than that from pure solvent.

G. L. CLARK

Interfacial tension. I. The statical measurement of interfacial tension in absolute units. WM. COLEBROOK REYNOLDS. *J. Chem. Soc.* 119, 460-5(1921).—An app. is described by which interfacial tension may be measured by a statical method. It consists essentially of a capillary tube centered inside of a buret by short fused rods. A water jacket for temp. control surrounds the buret, to the lower end of which is connected a tube of similar bore and a stop-cock. In making a run, e. g.,  $C_6H_6-H_2O$ , the buret is completely filled with  $H_2O$ . The tap is opened sufficiently to allow the level of  $H_2O$  to fall very slowly. As it falls  $C_6H_6$  is poured in to maintain the level until it finally enters the capillary. The interfacial tension  $T$  is calcd. from  $T = dghh'(D'-D'')/4h''$ , where  $d$  is the diam. of the tube,  $g$  is 981,  $h$  the difference in height in scale divisions of the buret of liquids in the 2 tubes,  $h'$  the capillary rise of  $H_2O$  in cm.,  $h''$  the same in scale divisions,  $D'$  the density of  $H_2O$ , and  $D''$  that of  $C_6H_6$ . The author is of the opinion that dynamic or drop methods give results for interfacial tension which must be multiplied by a factor of 1.26 to give the true values which he claims are obtained by the above method. II. The relation between interfacial and surface tension in sundry organic solvents in contact with aqueous solutions. *Ibid* 466-76.—Exptl. work on interfaces is tabulated in support of the law enunciated here that the interfacial tension between 2 liquids  $A$  and  $B$  is the difference between the surface tension of  $A$  satd. with  $B$  and that of  $B$  satd. with  $A$ . Exceptions are immiscible liquids that react chemically, Hg and liquid amalgams in contact with certain electrolytes, and old interfaces where adsorption has occurred. (The author has apparently overlooked the work of Harkins and his students which covers the same field considerably more rigorously. Abstractor.)

G. L. CLARK

Calculation of the diffusion constant of dissolved substances. HANS VON EULER AND ARVID HEDELIUS. *Z. anorg. allgem. Chem.* 113, 59-68(1920).—Expts. have been made to ascertain to what extent the presence of other substances influences the velocity of diffusion of a given substance, and a method is devised whereby the diffusion const. may be calcd. in the case of moderately concd. solns. The method is expressed by the



following rule. The diffusion const. of a soln. of a given concn. obtained experimentally is multiplied by the coeff. of viscosity of a soln. of  $1/4$  the concn. of the original soln. and divided by the relative osmotic pressure of the dil. soln. Curves are given for the variation of the relative viscosity with concn., and the relative osmotic pressure with concn. for solus. of sucrose of concns. 0-1*N*.

J. C. S.

Specific gravities of mixtures of butyl alcohol and water. Y. D. WAD AND A. G. GOKHALE. *J. Ind. Inst. Sci.* **4**, 17-25(1921).—The sp. gravities of mixts. of butyl alc. and water covering the entire range of miscibility were detd. at temps. of 20° and 25° and from the results curves were made and tables are given showing the sp. gravities of aq. butyl alc. of all concns., from which the following figures are taken:—

% Water.	Sp. gr. at 20°.	Sp. gr. at 25°.	% Water.	Sp. gr. at 20°.	Sp. gr. at 25°.
0.0 ..	0.8096 ..	0.8066 ..	18.5 ..	0.8448 ..	—
5.0 ..	0.8200 ..	0.8159 ..	94.5 ..	—	0.9886
10.0 ..	0.8292 ..	0.8258 ..	95.0 ..	0.9908 ..	0.9893
15.0 ..	0.8384 ..	0.8346 ..	97.5 ..	0.9942 ..	0.9931
17.5 ..	0.8429 ..	0.8395 ..	100.0 ..	0.9983 ..	—

J. S. C. I.

Connection between the limiting (electrical) conductivity  $\lambda_{\infty}$  of binary electrolytes in non-aqueous solvents and the viscosity  $\eta_{\infty}$  of the latter:  $\lambda_{\infty} \cdot \eta_{\infty} = \text{constant}$ . P. WALDEN. *Z. anorg. allgem. Chem.* **113**, 85-97(1920).—From a consideration of a large amt. of data previously published by W. and others, and a small amt. of new data, it is shown that the product  $\lambda_{\infty} \cdot \eta_{\infty} = \text{const.}$  for a large number of acids and some salts in non-aq. solvents. This rule holds for mixts. of solvents as well as for individual solvents. Water also obeys this rule when mixts. of solvents poor in water are considered, and when aq. solns. of electrolytes with highly complex ions are considered. The temp.-coeffs. of the viscosity and the limiting cond. are practically identical, that is,  $1/\lambda_{\infty} \cdot d\lambda_{\infty}/dt = -1/\eta_{\infty} \cdot d\eta_{\infty}/dt$ , or the empirical rule  $\lambda_{\infty} \cdot \eta_{\infty} = \text{const.}$  is independent of the temp. and the nature of the solvent over the temp. range 0-50°. The abs. value of  $\lambda_{\infty} \cdot \eta_{\infty} = k$  depends on the nature of the electrolyte, and in the case of binary electrolytes varies between 0.5 and 1.0. Variations from the rule are found in solvents which have a high viscosity or which show a high mol. association; in these cases, the mols. of the solvent are relatively large, and will change their size with changes of temp. or concn., and thereby change the degree of solvation of the electrolytes. Among such solvents are to be numbered glycerol, ethylene glycol, formamide, and mixts. of these with water,  $\text{SO}_2$ , and  $\text{NH}_3$ .

J. C. S.

Hydrodiffusion of ammonium magnesium sulfate and the separation of the component salts. C. PORLEZZA. Univ. Pisa. *Gazz. chim. ital.* **50**, 11, 289-906(1920).—In continuing a study of  $\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  P. has studied its behavior on diffusion in aq. soln. with the idea of using data obtained in the Tuscan boric acid industry, where this salt is present as a by-product of little value. In the large literature on diffusion there is little concerning this salt. Expts. by Torrance and Knight (*C. A.* **12**, 2475), and by Maxwell (*C. A.* **12**, 329) are discussed but P. has preferred to use the method of successive strata (Göholm, *Z. physik. Chem.* **50**, 309(1905)). The numerical data are given in tables. The results give for  $K_{\text{MgSO}_4}$  0.280 and for  $K_{(\text{NH}_4)_2\text{SO}_4}$  0.696 in this double salt.

E. J. WITTEMAN

Ionic velocities in non-aqueous solutions. P. WALDEN. *Z. anorg. allgem. Chem.* **113**, 113-24(1920).—A theoretical paper, in which from previously published data W. shows that the product of the ionic cond. and the viscosity of the solvent is a const. quantity,  $l_{\pm} \times \eta_{\infty} = \text{const.}$ , and  $l_{\pm} \times \eta_{\infty} = \text{const.}$  The velocities of the ions are inversely proportional to the viscosity of the solvent, and these products are independent of the



temp. It is also shown that the transport number at infinite diln. is practically the same as that at any other diln. for dil. solns. For one and the same ion in different solvents the same transport number is obtained. Aq. solns. of various ions with the exception of the H ion give the same transport numbers as non-aq. solns., and in general it may be said that in high dilns. with highly dissociated binary electrolytes the transport numbers of a given ion are independent of the nature of the solvent and of the temp. This is expressed by the equation  $l_{\infty}\eta_{\infty}/(l_{\infty}\eta_{\infty} + l_{\infty}\eta_{\infty}) = n_{\infty} = \text{const. } k_1$ . J. C. S.

**Diameter of ions in non-aqueous solutions.** P. WALDEN. *Z. anorg. allgem. Chem.* 113, 125-30 (1920).—A theoretical paper, in which, by means of Einstein's formula,  $U = K/N \cdot 6\pi\eta\rho$ , in which  $U$  is the velocity of a particle,  $K$  the force acting on a particle,  $N$  the Avogadro number,  $\eta$  the coeff. of viscosity, and  $\rho$  the radius of the particle, the radius of a number of ions in MeOH soln. has been calcd. It is shown that for most ions the value of  $\rho$  lies between  $2.0 \times 10^{-8}$  cm. and  $3.9 \times 10^{-8}$  cm. H has a smaller value,  $1.1 \times 10^{-8}$ , and Li a larger value,  $4.70 \times 10^{-8}$  cm. The ionic radius in non-aq. solvents follows the same order as in aq. solns., namely,  $\text{H}^+ < \text{K}^+ < \text{Ag}^+ < \text{Na}^+ < \text{Li}^+$  and  $\text{Br}^- < \text{I}^- < \text{Cl}^- < \text{NO}_3^-$ . In the case of the above-named simple ions the ionic radius in aq. solns. and the at. radius are practically the same except in the extreme cases H and Li, while in non-aq. solns. the values of the ionic radius are about twice as great. The mean values obtained are, in aq. soln.  $2.67 \times 10^{-8}$  cm., and in non-aq. soln.  $5.33 \times 10^{-8}$  cm. A further set of ions, consisting of org. anions and cations, has the same ionic radius in both aq. and non-aq. solns., the mean value in this case being  $4.4 \times 10^{-8}$  cm. The difference in the radius in the case of the simpler ions is held to indicate a much greater solvation in non-aq. solvents than in water. J. C. S.

**The theory of electrolytic ions. XVIII. Mobility and space-filling of arsinic acid ions.** RICHARD LORENZ AND ERIKA SCHMIDT. *Z. anorg. Chem. allgem.* 112, 269-77 (1920).—The conductivities of the Na salts of a number of substituted phenylarsinic acids (cf. *C. A.* 15, 2379) have been used to calc. the ionic mobilities of the corresponding anions. The upper and lower limits of the ionic mobilities were also calcd. from the "space-filling numbers," and in every case the mobility calcd. from the cond. was below the lower limit calcd. from the space-filling number (cf. *C. A.* 14, 3353). The densities of the free acids were detd. at 20°, and the following values are given: arsanilic, 1.9571; *o*-aminotolylarsinic, 1.7475; *o*-diaminophenylarsinic, 1.8313; dimethylaminophenylarsinic, 1.6746; *m*-dihydroxyphenylarsinic, 2.0040; 3-nitro-4-aminophenylarsinic, 2.0359; dichlorohydroxyphenylarsinic, 2.1020; dibromohydroxyphenylarsinic, 2.4150; 3-nitro-4-hydroxyphenylarsinic, 2.0314; *p*-phenylenediarsinic, 2.2025; dinitrohydroxyarsinic, 2.0565. Kopp's law was applied to calc. the at. vol. of As in these compds., but results ranging from 11.2 to 33.3 were obtained from different compds.

**XIX. Determination of the size of the benzene nucleus from [electrical] conductivity.** RICHARD LORENZ. *Ibid.* 113, 131-4 (1920).—The radius of an ion and its mobility at 25° are connected by the expression  $\mu = 1/\tau_{\infty} \times 89.34 \times 10^{-8}$ ; making use of this expression, the authors have calcd. the ionic radii of the various anions of the substituted arsinic acids from data previously published (*C. A.* 15, 2379). It is found that the univalent ions have about the same radius,  $3.83 \times 10^{-8}$  cm., the bivalent  $4.40 \times 10^{-8}$ , the trivalent  $4.68 \times 10^{-8}$  cm., while the *p*-phenylenediarsinic ion has a radius  $7.0 \times 10^{-8}$  cm.. From these figures, it is concluded that the value  $6.2 \times 10^{-8}$  cm. found by Debye is too large for the radius of the benzene nucleus, while  $1.45 \times 10^{-8}$  found by Fajans (*C. A.* 14, 3086) is too small. **XX. Hertz's theory of ionic mobility.** *Ibid.* 135-40.—A theoretical paper in which the consts.  $A$  and  $A'$  of Hertz's theory of ionic cond. (*C. A.* 6, 955) are numerically evaluated and brought into a suitable form for general use. These have the form  $A' = 167.7/T^2 \times 10^3$ , and since  $A = \sqrt{A'}$ ,  $A = 5515/T$ . An expression has been evolved for multivalent ions, and this has the form  $A' = t^2 \times 167.7/T^2 \times 10^3$  and



$A = v^2 \times 5515/T$ , where  $v$  is the valency. The relationship between the ionic mobility and the cond. is discussed, and it is shown that only when the cond. is regarded as a function of the concn. can a Hertz curve be constructed if the  $A$  constant is regarded as a universal constant, as is demanded by the theory. **XXI. A first proof of Hertz's theory of conductivity.** RICHARD LORENZ and PHILIPP OSSWALD. *Ibid* 114, 209-233.—The conductivities of aq. solns. of AcONa were detd. with an accuracy of 0.1%. From the numerous points on the curve of cond. plotted against concn., it was possible to test the empirical laws of extrapolation to infinite diln. and the law of Hertz (*C. A.* 6, 955). The two empirical equations of Kohlrausch were found to break down, but the results agreed extremely well with Hertz's theory. The values at infinite diln. for AcONa were calcd. as:  $10^\circ$ ,  $\mu_0 = 63.15$ ;  $18^\circ$ ,  $\mu_0 = 76.56$ ;  $25^\circ$ ,  $\mu_0 = 90.05$ . The abs. value of the universal const. in Hertz's formula was not confirmed, although its change with temp. agreed approx. with the theory. The const. is not universal, but must be found for each electrolyte. J. C. S.

**Theories of electrolytic ions. XXII. Transference velocity of a single ion. A second proof of the theory of ionic conduction of Paul Hertz.** R. LORENZ AND W. NGU. *Z. anorg. allgem. Chem.* 116, 45-61(1921); cf. preceding abstr.—By means of an improved form of the ionic transport app. developed by Whetham and Nernst the ionic velocity of  $\text{MnO}_4^-$  has been measured at  $18^\circ$  and  $25^\circ$ ,  $\text{BrO}_4^-$  at  $18^\circ$ ,  $\text{F}^-$  at  $18^\circ$ ,  $\text{IO}_3^-$  at  $25^\circ$  and  $\text{ClO}_3^-$  at  $18^\circ$ . The data are given in tabular form. The results bear out the theory of Paul Hertz. E. H. DARBY

**Methods of stating acidity.** EDGAR T. WHERRY AND ELLIOT Q. ADAMS. *Bur. Chem. J. Wash. Acad. Sci.* 11, 197-9(1921).—Both concn. and potential methods are in general use for stating effective acidity and alkalinity. The concn. method is easier to understand, and "may be recommended to writers who wish to make their data readily comprehensible." The discussion is based, however, on the potential methods,  $X_H$  and  $P_H$ . The usefulness of methods in which computation begins at the neutral point  $X_H$  has been urged by several writers. W. M. Clark has recently in a book on detg. H-ions raised objections to such methods, which are here answered. He holds that they involve assumptions as to the nature of pure  $\text{H}_2\text{O}$  which is actually never used. It is pointed out that the  $P_H$  method of statement involves assumptions as to the nature of a hypothetical acid which is completely ionized in normal soln.; and that "such an acid is at least as imaginary as is pure water." Moreover on the alk. side the  $P_H$  method does involve the data for pure water, so that the entire error which may exist in such data is referred to the alk. range, whereas in a method starting at neutrality it is evenly divided. C. holds that  $P_H$  values are more directly derivable from the potential of the H electrode, but it is noted that both methods are indirectly based on a half-cell. C. records that workmen can be taught to use the  $P_H$  system (without understanding it). It is remarked that so can chemists be taught to use the Baumé scale and other empirical atrocities. C. urges that quantities of important data are already recorded in terms of  $P_H$ , to which it is replied that changes in methods of recording data are not unknown in the history of chemistry. Finally, it is pointed out that the  $P_H$  system, based on the validity of the laws of dil. solns., takes its origin in the very region (normal solns.) in which those laws do not hold. E. T. W.

**Reply to Wherry and Adams' article on methods of stating acidity.** WM. MANSFIELD CLARK. Hygienic Lab. *J. Wash. Acad. Sci.* 11, 199-202(1921); cf. preceding abstract.—The practical difficulty of changing the data already in thousands of cases recorded in the  $P_H$  system is reaffirmed. It is held not to be desirable to simplify methods of stating acidity for workers in non-mathematical sciences, for in so doing one "covers up those logarithmic relationships which it is of inestimable value to impress upon the student." However, the real source of difference in point of view is found in



W. and A.'s answer to the first point (concerning the relative reality of pure water and completely ionized normal acid). "There the point of view of a theorist seems to be confused with the point of view of an experimentalist." Since the exptl. methods of detg. reaction are based on the H electrode, it is desirable to use  $P_H$  values, which are a linear function of the p. ds. throughout the scale, rather than to divide the scale up into "a region of 'acidity' and a region of 'alkalinity' divided from one another by the theoretical neutral point." The fact that the continuity of the  $P_H$  scale at the "neutral" point agrees with the actual conduct of the H electrode and of equilibria at that point is considered to be a point in favor of this scale. In the use of the dissociation const. of bases it may be necessary to introduce the dissociation const. of  $H_2O$ , but only in a limited number of cases, and not at the very outset as is done in any system starting at the neutral point. The  $X_H$  scale presents to the student a symmetrical picture, but the  $P_H$  scale emphasizes the exptl. derivation of the values and the continuity of equilibria. The setting up of a new reference point—the H-concn. of water instead of that of normal acid—is therefore held to be undesirable.

E. T. W.

**The molecular directing force in liquid crystals.** O. LEHMANN. *Z. anorg. Allgem. Chem.* 113, 253-305 (1920).—A theoretical discussion of the properties of different kinds of fluid crystals, as revealed by their optical behavior. The properties are best accounted for on the assumption that the fluid crystals have a leaflet-like structure, the units of which endeavor, as far as possible, to remain parallel, but can glide freely in a direction parallel to their faces (cf. *C. A.* 15, 1429).

J. C. S.

**Equilibria of hydrofluosilicic acid.** LAWSON J. HUDLESTON AND HENRY BASSETT. *J. Chem. Soc.* 119, 403-16 (1921).—The present accepted method of testing for silica in HF by adding KCl with formation of turbid  $K_2SiF_6$  is found to be inadequate. A method of studying the compn. of mixts. of HF and  $H_2SiF_6$  is found in the fact that for the complete neutralization of the latter acid according to the equation  $H_2SiF_6 + 6NaOH = 6NaF + H_2SiO_3 + 3H_2O$ , an appreciable time is required. Thus when NaOH is added to the mixed acids the time may be measured from the moment of mixing till the color of the indicator (phenolphthalein) fades. Other additions of alkali are made until the color no longer fades. Since the total concn. of H ions is produced but slowly, they must be bound in a complex. If  $n$  cc. of alkali were originally present and  $N$  cc. were required for the total permanent neutralization  $(N-n)/N \times 100 = C$  is the percentage of total H ions in bound condition at the moment of fading. The various values of  $\log C$  plotted against time give the straight line usual for amonomol. reaction, from which  $C_0$ , the original concn. of the complex present in the unneutralized acid, is calcd. The rate of disoc. of  $Na_2SiF_6$  into  $SiF_4$  and  $NaF$  is detd. The effect of temp. upon the velocity const. is given by the equation  $\log k = -10662/T + 29.83$ . Equil. conditions demand that when  $SiF_4$  is passed into  $H_2O$  a considerable proportion of unchanged  $SiF_4$  should be present, and that  $H_2SiO_3$  can exist in soln. with an active mass proportional to its concn. to the extent of at least 0.003 mol. per l. at 15°.

G. L. CLARK

**Kinetics of the ketonic decomposition of acetoacetic acid.** ERIK M. P. WIDMARK. *Acta med. Scandinav.* 53, 393-421 (1920).—The course of the reaction is followed by estn. of the  $CO_2$  evolved according to Winckler's method (pptn. of  $BaCO_3$ ). The necessary acetoacetic acid is prepd. by hydrolysis of technical Et acetoacetate by alkali hydroxide, this process being complete before acetone is produced in measurable amt. The formation of acetone has been investigated in acid and alk. soln.; in the latter, practically only the electrolytically dissociated anion of acetoacetic acid is present, since the salt is extensively dissociated into  $Na^+$  and  $CH_3COCH_2CO_2^-$ . In strongly acid soln., on the other hand, the acid is present as such, since electrolytic disoc. can be neglected. It is found that the undissociated and dissociated acids exhibit greatly differing rates of decomn., that of the former being about 50 times greater. In



alk. soln., formation of acetone occurs at the rate of decompn. of the anion, the velocity of which is calcd. from a series of concordant observations to be 0.00008 at 37°; in strong mineral acid soln., on the other hand, it occurs at the rate of decompn. of the acid itself, the const. of which is calcd. to be 0.0042 at 37°. As is to be expected, the reaction is of the first order in either case. In almost neutral solns., in which the acetoacetic acid is partly dissociated, the rate of decompn. depends on the degree of electrolytic dissoc. and can be calcd. from the expression  $\alpha V_1 - (1 - \alpha) V_\infty$  ( $V_1$  and  $V_\infty$  = consts. of decompn. of the ion and undissociated acid resp.;  $\alpha$  = degree of dissoc.). This expression is valid for all concns. of H ions. On the other hand, the degree of dissoc. depends on the H-ion concn., which varies with the progress of the action, since acetoacetic acid is decomposed. In spite of these complications, W. has succeeded in establishing the validity of his hypothesis; in nearly neutral soln., the velocity const. gradually diminishes, in consequence of falling H-ion concn., and the extent to which this occurs harmonizes well with the theoretical calcs. On the other hand, the H-ion concn. can be maintained const. by the addition of AcOH and AcONa, and in this case the velocity const. becomes uniform. Under these conditions, the H-ion concn. can be estd. by a study of the rate of reaction, and the value thus found is identical with that detd. by electromotive measurements.

J. C. S.

**Solubility of sulfur in cold caustic alkalis.** G. CALCAGNI. R. Ist. tecn., Venice. *Gazz. chim. ital.* 50, II, 331-40 (1920).—In the prepn. of  $(\text{NH}_4)_2\text{S}_x$  by the ordinary method C. observed that powdered S added to cold  $\text{NH}_4\text{OH}$  is readily dissolved. This soln. becomes yellow and then in a few days becomes colorless. During this period the bottle was opened several times and S was sepd., but not all, since the addition of acid gives a ppt. of milky S due to the presence of sulfides and thiosulfate. After making these observations C. decided to study the soly. of S in caustic alkalis and to see if light exercises any catalytic action. A review of the literature shows that earlier workers have studied the action of hot alkalis on S and have tried to establish a single equation. C. believes that such a single reaction for all alks. can not be established but that there is a series of reactions depending on the concn. and other conditions. 200 cc. of 66% KOH and NaOH,  $\text{NH}_3$  (d. 0.888), satd. cold  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ , and satd.  $\text{Mg}(\text{OH})_2$  in the presence of MgO were treated with freshly powdered S. In NaOH and KOH the color became quite intense but in the others the soln. was slower. This was due to the greater concn., since in 10, 20, 30, 40 and 50% KOH and NaOH the soln. in all but the 50% soln. was quite slow and the color gradation was proportional to the alk. concn. Five g. S were soon dissolved in the 50% soln. and more was added to keep an excess present. These solns. in KOH, NaOH and  $\text{NH}_4\text{OH}$  were dark red but on standing became clearer and sepd. a black powder that was black S. In all of these processes light had no observable effect. In all cases the solns. were analyzed and the results are given. In 100 cc.  $\text{Ca}(\text{OH})_2$  soln. 0.1116 g. S were dissolved. After a certain S addition to  $\text{Ba}(\text{OH})_2$  soln. beautiful crystals were sepd. and when this stopped the soln. was analyzed. The ratio was 137.4 of Ba (1 atom) : 189 of S or 100 cc. satd.  $\text{Ba}(\text{OH})_2$  dissolved 2.60 g. S. The crystals were  $\text{BaS}_4$ . With  $\text{Mg}(\text{OH})_2$  solns. in the presence of S the ratio was 1 atom Mg: 2 atoms of S or 100 cc. of satd.  $\text{Mg}(\text{OH})_2$  dissolved 0.014 g. S. All the above solns. gave reactions of sulfides, polysulfides, thiosulfates and sulfites. The last 2 are most abundant in the solns. of KOH, NaOH and  $\text{NH}_3$ ; the  $\text{Ca}(\text{OH})_2$  contained traces of the latter. The  $\text{Ba}(\text{OH})_2$  soln. gave a faint test for thiosulfate but no test for sulfite. The solns. of S in  $\text{NH}_3$  reacted in every way like the usual polysulfide reagent. The S is first dissolved in these alk. solns. to give sulfides which then give rise to thiosulfates and by further soln. of S the various polysulfides are formed. The S of thiosulfates is partly deposited and gives the sulfites. In more concd. solns. the S is partly in true soln. as was shown by extg. some of it with  $\text{C}_6\text{H}_6$ . With the  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}$



(OH)<sub>2</sub> solns. of S the CO<sub>2</sub> of the air caused the pptn. of carbonates. Test expts. showed that CO<sub>2</sub> decomposes the sulfides with the evolution of H<sub>2</sub>S and the pptn. of S. The solns. of the KOH, NaOH and NH<sub>3</sub> are similarly decomposed by CO<sub>2</sub> and decompn. products differ according to the concn.: in dil. solns. the S is largely sepd. as such and little H<sub>2</sub>S is evolved; in concd. solns. the reaction is slower and nearly all the S is evolved as H<sub>2</sub>S. The fact that CO<sub>2</sub> expels the S from these solns. proves that the soly. of S in the alkalies is not due to the presence of carbonates in soln., since the formation of these compds. causes the expulsion of S from the soln. C. has found that Se is sol. in NaOH and is studying this.

E. J. WITZEMANN

**Chemical kinetics.** UGO PRATOLONGO. *Gazz. chim. ital.* **48**, I, 121-82(1918); *Chem. Zentr.* **1919**, I-II, 421-3.—Chem. kinetics constitutes a problem in general dynamics which is connected with statistical mechanics. From the latter point of view the speed of reaction is accounted for as depending upon the no. of mols. whose energy has exceeded a definite critical value. This is the fundamental basis of the work of Marcelin upon this subject, originally developed in *Ann. physique* (C. A. **9**, 1710). The method used in the present paper is the statistical mechanics of Gibbs. As a condition of reaction capacity a fixed mol. energy follows which in this Gibbs system has a precise meaning which should have been given to it formerly. This is designated as *crit. energy*. For the coeff. of reaction velocity  $k$  there is developed the

formula  $k = e^{\frac{\psi_0 - \epsilon}{\theta}} + \text{const.}$  in which  $\psi_0$  is the av. mol. energy at abs. 0, and  $\epsilon$  the crit. energy at the obs. abs. temp.  $\theta$ . This formula has the form of the exptly. based expressions for the same coeff. derived by van't Hoff and Arrhenius. For increasing temp., the coeff. of reaction velocity should, according to this formula, increase from zero, reach a maximum and then again asymptotically approach zero. A special role is played in the theory by the difference between the av. mol. energy and the critical energy,  $\psi_0 - \epsilon$ , which is designated by the name *relative critical energy*. A break in the temp. curve of the temp. coeff. called for by the theory is too slight to be recognized exptly. The ordinarily expressed ratio of the temp. coeffs. for a rise in temp. of 10° should rise from zero to a very large value and approach the value 1. This is strictly true only for reactions in gaseous systems. The exceptions in aq. soln. are to be ascribed to the abnormality of the solvent, as it shows itself, for example, in the density max. of H<sub>2</sub>O. At a given temp. the slower reactions, which are characterized by a larger relative critical energy, have the larger temp. coeffs. The formula thus set up for the coeff. of reaction velocity granted, it is at once possible to calc. the relative critical energy for isolated reactions as independent of temp. and, for the isolated reaction as such, entirely characteristic. It expresses the total energy which must be supplied to each mol. in a system in order to take it over from the ordinary to the reactive condition. Thermal units are used for the energy expressions. The highest values of the relative critical energy are obtained for inactivating reactions of org. toxins and enzymes, which can indeed be considered as typical chem. reactions. The values of the energy increased from 0 to 100,000 but in general are of the order of 10<sup>4</sup>. In addition to the type of reactions just mentioned, others considered in the present paper are vaporization, sublimation, several chem. reactions, photochem. decompn., etc. The temp. interval for each reaction is given, from which the observations have served for calcn. A higher relative critical energy in general corresponds to the gas reactions which go to completion in the absence of a solvent and in the dil. state, than that which corresponds to the same reactions in a solvent, in the presence of a catalyzer, or under the influence of light. For isolated photo-chem. reactions the total energy goes down even to 0. This change in total energy according to the conditions is an indication that the same reaction may complete itself in very different ways. The typical influence of solvent, catalyzer and



light is illustrated by a series of examples, viz.: decompn. of  $H_2O_2$ , hydrolysis of maltose and sucrose, oxidation of  $HCHO$  with  $H_2O_2$ , oxidation of  $HI$  in aq. soln., action of  $Cl$  on  $C_6H_6$ , saponification of the glycerides of  $AcOH$  and of  $Et$  acetate, lipolysis by pancreas lipase, etc. A diminution in wave length of light results, according to researches on phototropic reactions, in a decrease of the relative critical energy of the reaction. Equilibrium, since it is the point of equality of 2 opposed reaction velocities, may, therefore, be fundamentally considered from the point of view of Gibbs' mechanics. In view of the equality of the crit. energies of the 2 opposed reactions, an equilibrium

coeff. of the form  $K = e^{\frac{\psi_1 - \psi_2}{\theta}} + const.$  is obtained. Here  $\psi_1 - \psi_2$  refers to the heat of reaction within the limits of practicability of the reactions already considered as applying. The catalytic, photochem., and solvent effects which constitute a common group result from a change of the av. mol. energy or critical energy of the reaction by virtue of the presence of these effects. The change of critical energy is characteristic of these effects which change only the velocity, not the equil. Changes also of equil. are detd. by the change of  $\psi_1 - \psi_2$ . This means that the heat of reaction must also change if the equil. should be affected. The catalytic and related phenomena will be divided into 2 classes, according as the equil. remains unchanged or shifts. Special consideration is given to the so-called poisoning phenomena of catalyzers. This action stands midway between catalytic and enzymic effects. The poison can combine with the reacting substance and thereby give rise to a new reaction designated as parasitic, which seeks to restore the system to its original condition, and by so doing poisons even the catalyst. The poison can be considered as a kind of powerful and active catalyst with a smaller value of the crit. energy in proportion to the principal reaction. A second possibility as to the role of the poison is also considered. Both dispose of the poisons under catalytic actions of the first class. By consideration of poisoning from the standpoint of catalytic reactions of the second class, the possibility of an insight into negative catalysis is presented. Turning to photochem. reactions, the observation serves as a starting point that every photochem. absorption is accompanied by chemiluminescence. For the catalytic, photochem. and solvent effects of the first kind it must be accepted that the reduction of crit. energy should be connected with an intermediate reaction. From the standpoint of kinetics several observations are made upon such phenomena as the nascent state, "Rest-strom," overvoltage, etc. It turns out that the Boltzman energy partition, at least in the main, is susceptible of direct exptl. confirmation. In the consideration of the relation of chem. kinetics to thermodynamics, the irreversible chem. processes are classified as a third group to the irreversible and reversible physical processes. In an elementary chem. process it is

possible to consider the entropy lowering as measured by the quotient  $-\frac{\psi - \epsilon}{\theta}$ . A photochem. reaction of the second kind is accepted within the assimilation, which possesses a considerable critical energy—a thing which differentiates it from ordinary photochem. processes. Chem. processes with which here vaporization, sublimation, condensation, etc. may also be reckoned, can be conceived of as a selection among the mols. whereby only those are selected which possess a high energy content. Whence the possibility of processes shall be given which proceed with entropy lowering. G. L. CLARK

- The catalytic oxidation of ferrous salts in acid solutions. RICHARD THOMAS AND EDWARD T. WILLIAMS. *J. Chem. Soc.* 119, 749-58 (1921).—Sols. of  $FeCl_2$  were shaken with  $HCl$ ,  $O$ , and  $NO$  (liberated *in situ* from  $NaNO_2$ ), and the rate of absorption of the  $O$  at atm. pressure was measured. This rate was always inversely proportional to the concn. of  $FeCl_2$ , so that oxidation proceeds with acceleration despite the fact that the active mass of the substance undergoing oxidation is decreasing. Autocatalysis by the



$\text{FeCl}_3$  produced is out of question. After discussing the results in relation to theories of catalysis, the authors conclude that adsorption *per se* does not det. chem. reactivity, and that in catalytic reactions, the existence of a compound or complex between the catalyst and one of the reacting substances is not evidence of itself that such compound formation is the mechanism by which the reaction proceeds. "The mechanism of the catalytic action of NO on the oxidation of ferrous salts by air or O is the oscillation of the oxide of N between two states of oxidations."

JEROME ALEXANDER

**The general study of catalysis.** MARCEL GUTCHARD. *Bull. soc. chim.* 29, 212-4 (1921).—The study of catalytic reactions, especially in heterogeneous gas-solid systems, has not passed entirely the empirical stage. Such non-precise expressions as, "support," "activator," and "catalytic poison" scarcely mask the relative poverty of our knowledge. The best way of making progress in the study of catalysis is not to make catalyses, but rather to study independently the elementary phenomena which probably take part in catalytic reactions, thereby laying a foundation of facts upon which a productive theory can be built. From this point of view the following lines of research seem to be particularly indicated. The study of the diffusion of gases into each other. The diffusion of gases into solids, particularly metals. The variation of the surface due to reversible allotropic changes in the case of certain metals, or irreversible ones in the case of certain oxides. Changes in surface due to the formation of compds., many of which probably have not been isolated. The study, by means of adsorption phenomena, of the variation of the surface of powders. The size of the grains is probably not a matter of indifference, and the relation between the surface and vol. may influence the reaction velocity. One of the principal difficulties in the study of gas-solid catalysis is the detn. of the actual duration of the contact between gas and solid. Usually one knows only the possible duration of contact as detd. by the time required for a unit vol. of gas to pass the space occupied by a unit vol. of the catalyzer. Even here, the space which it is necessary to know is that between the grains of the catalyzer. If the grains are not spheres this space should be detd. directly. The choice of uniform grains is merely an approximation.

R. H. LOMBARD

**Topochemical reactions. The formation of carbon on contact substances.** V. KOHLSCHÜTTER AND A. NÄGELI. *Univ. Bern. Helvetica Chim. Acta* 4, 45-76 (1921).—According to the X-ray spectrographs of Debye and Scherrer, graphite consists structurally of C mols. linked together in planes, these planes being superimposed and bound together vertically. Thus the formation of graphite should be a topochemical reaction, occurring when the local conditions imposed upon a C-forming reaction favor the production of such a structure. Also, the graphite should bear the stamp of the topochemical conditions which were effective in producing it, i. e., it should mirror in some way the characteristics of the place of reaction. If the topochem. conditions are unfavorable for the formation of the graphitic structure, other things being equal, the same reaction should yield amorphous C. To test this viewpoint, K. and N. have studied the nature of the C deposited upon electrolytic films of Co, Ni, Fe, and Ag, and upon powders of these metals, by the reaction  $2\text{CO} = \text{C} + \text{CO}_2$ , at about  $500^\circ$ . The supporting metal upon which the catalytic metals are electrolytically deposited influences the amt. of C formed, it being greater when the support is Pt, and less when Ag or Cu. The nature of the catalytic metal det. specifically the method of deposition, the amt., and the characteristics of the C. In the case of smooth Co, Ni, and Ag deposits the C is not deposited visibly upon the surface, but in the interior of the metallic film, and appears as an unweighable film when the metal is dissolved in acid. In the case of Fe, however, the C forms a deep-black surface deposit. Co affords the largest C deposit, then Ni, Fe, and Ag. The C deposited on Co is strongly graphitic; on Ni also graphitic, but somewhat more easily oxidizable; on Fe more sooty, and still more easily oxidizable;



and on Ag very small in amt., but difficultly oxidizable. The combination of the Pt support and catalytic metal also seems to play a part in the reaction, because a considerable C deposit takes place only when they are strongly adherent; the Pt foil support appears attacked after the reaction, suggesting a possible dissolving of the CO in the Pt and a consequent conen. of it; and the C film is very strongly adherent to the Pt. Often, too, the Pt is contaminated with Ni, suggesting a welding together of the two. The structure of the electrolytic deposit of catalytic metal determines the appearance of the C, and its chem. behavior as indicated by its action toward oxidizing agents. On dark, lusterless deposits the C is deposited visibly on the surface, as was the case with smooth deposits of Fe; and it is more easily oxidized than C deposited within the metallic layer. On smooth, coherent, shiny surfaces of Ni, Co, or Ag, no C is deposited visibly, but it becomes evident only when the metallic film is dissolved in acid. This C film is graphitic, its form corresponds to that of the dissolved metallic deposit, and its surface adjacent to the Pt support is mirror-like when it can be detached. Smooth metallic deposits sometimes also contain roundish granular or nodular excrescences which occur especially when a. c. is imposed upon d. c. during the deposition. On such denser and thickened areas no C is deposited, either on the surface or within the metal; and the C film left after dissolving the metallic deposit has holes in it which correspond to these areas. The amt. of C left after dissolving the metallic layer is detd. by the sp. action of the combination of catalytic metal deposit and its support, and by the thickness of the metallic deposit, rather than by the duration of the CO treatment. With minimum thickness of the deposit the C film is extraordinarily fine and appears to have replaced the metallic layer. As the thickness of the metallic layer increases, the amt. of C soon reaches a max. The following explanation of the above phenomena is suggested. The innermost layer of the electrolytic deposit, next to its support, consists of an extremely fine, disperse network of crystallites, possibly arranged more or less in layers parallel to the electrode surface as a result of the contractile forces present during its formation. Above, nearer the surface, the structure is more dense and less disperse. The max. catalytic effect would occur, as observed, at the greater surface of the inner layer, and the stratified structure of this portion of the metallic deposit and the intercrystalline pressure are favorable for the formation of the graphitic structure. Possibly the formation of graphite does not occur until the metal is dissolved, permitting the parallel C planes to unite. Expts. with metallic powders substantiate these results. In the case of *Ferr. Pulv.* and *Ferr. Red.* the former yielded a more graphitic C than the latter, corresponding to the greater contact surface of the particles of the former. The graphitic nature of the C increased with rising temp., from 300° to 500°. The amt. of C produced by metallic powders was large, almost filling the reaction tube, and it was almost inseparably associated with fine particles of the metal. *Niccol. Red.* gave abundant C, of about the same graphitic character as that by Fe. *Cob. red.* gave a voluminous deposit of C, very different from that by Fe or Ni, and typically graphitic. The fact that the C deposited on Fe powder is very sooty, although graphitic, shows the possibility of the same reaction producing a continuous gradation of C between amorphous C and graphite, the nature of the product being detd. solely by the nature of the place of reaction. The significant difference between the topochem. conditions in metallic powders and in electrolytic deposits is that in the latter the closely united, stratified structure favors the development of the C deposit in layers, whereas in powders the particles are arranged loosely and irregularly, and the deposition of C in planes is more difficult. The C can become graphitic only along the surfaces of the particles, and only insofar as their surface extension is large. Also, the intercrystalline pressure is lacking in powders, and the particles of catalyst are forced apart instead of the C deposit being pressed together by them.

R. H. LOMBARD



**Influence of surface tension on fusion and solidification.** ERNST RIE. *Wien. Anz.* 1920, 137-9.—In connection with a communication by Pavlov (*C. A.* 3, 860) R. develops an expression for the dependence of the m. p.,  $T_s$ , of small, cryst. granules on the surface tension,  $S_m$  (free energy of the surface), in the form  $T_s - T_0 = -T_0 \times 2S_m / srg$ , where  $T_0$  is the limiting m. p. (without reference to surface energy),  $s$ , the density of the solid phase,  $r$  the radius of the cryst. granules considered as spheres, and  $q$  the latent heat of fusion. This expression, which is derived from the Gibbs equil. conditions by purely thermodynamic reasoning, and is readily adapted to the case of a drop enclosed within a crystal, gives results differing from those of Pavlov. Further observa-

tions of the m. p. of crystals are necessary to decide which of the conditions,  $S_m \geq S_m + S_m$  is valid. Probably, the majority of amorphous substances are composed of extremely minute crystals, the size of the granules being  $< 10^{-7}$  cm.; the absence of a definite m. p. is to be ascribed to surface tensions. J. C. S.

**A simple method for the determination of melting points and critical temperatures:** HERMANN RASSOW. *Z. anorg. allgem. Chem.* 114, 117-50 (1920).—An app. was devised for m. p. detns. consisting of a solid cylinder of Cu 10 cm. long and 5 cm. in diam, bored with an axial hole to a short distance below the center for taking the specimen, a parallel hole for a thermocouple, and a transverse hole intersecting the first hole at the center of the cylinder. Through the transverse hole the specimen, illuminated by a lamp placed opposite the other end, was viewed through a telescope. The cylinder was heated electrically by a winding of Ni wire. The substance to be examd. was sealed up in a tube of hard glass or transparent quartz, which was suspended through the axial hole in the field of view of the telescope. With this app. temps. up to  $1089^\circ$  could be obtained with a limit of error  $\pm 1^\circ$ . The following m. ps. were detd: KI,  $684.1^\circ$ ; KCN,  $601.2^\circ$ ;  $\text{NH}_4\text{Cl}$ ,  $519.7^\circ$ ;  $\text{NH}_4\text{Br}$ ,  $541.9^\circ$ ;  $\text{NH}_4\text{I}$ ,  $551 \pm 3^\circ$ , the accuracy being interfered with by dissoc.;  $\text{N}(\text{Me})_3\text{Cl}$ ,  $420^\circ \pm 10^\circ$ , much dissoc. occurring; As,  $818^\circ$ . Expts. were also made on the m. ps. of mixts. of  $\text{NH}_4\text{Cl}$  with halides of alkali metals. The method is not suitable for the detn. of complete m. p. diagrams of mixts., but serves to indicate whether miscibility of two salts is possible or not. With a quartz manometer on the principle of the Bourdon spiral, a detn. of the vapor pressure of  $\text{NH}_4\text{Cl}$  between  $340^\circ$  and  $520^\circ$  was made. At  $520^\circ$  the vapor pressure is 37.5 atms. The m. p. app. was also used for the detn. of some crit. temps. The results obtained were:  $\text{HgCl}_2$ ,  $704^\circ$ ;  $\text{HgBr}_2$ ,  $738^\circ$ ;  $\text{HgI}_2$ ,  $797^\circ$ ; S,  $1040^\circ$ ; I,  $553^\circ$ . The crit. temps. of As and Hg are above  $1400^\circ$ . J. C. S.

**Phenomena in the formation of space lattices composed of two different species of atoms, particularly in the formation of mixed crystals of silver and gold.** G. TAMMANN. *Z. anorg. allgem. Chem.* 114, 281-8 (1920).—When the sol component of a mixed crystal is removed, the atoms of the insol. residue may behave in 4 ways: (1) remain as an at. dust or conglomerate of particles with irregular at. grouping; (2) combine to microscopic crystals; (3) combine with the solvent or solute, although the substance in mass is not attacked; (4) combine together and attract other atoms to the chain. With mixed crystals of Au and Ag (and probably other metals), case (2) only occurs on extrn. with  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ . With mixed crystals of Pt with Ag or Cu, cases (2) and (3) occur simultaneously. The behavior of alloys of Pt with Pb, Bi, or Zn, contg. Pt compds., is similar. Mixed crystals of Fe with Si on treatment with HCl give only silicic acid. Si hydride is evolved when the Si is in combination with an electropositive metal, such as Mg, which forms  $\text{MgSi}$ . Fe-C mixed crystals give hydrocarbons with HCl. The residue of Au left after dissolving out the Ag from an alloy was found by X-ray examn. to be cryst., although it was finely divided and almost black. At higher temps., the particles are larger and yellow. The sepn. of Au and



Ag is described. The residue of Ag in the Au after treatment with acid is appreciable when the original alloy contains only small quantities of Ag, and increases as the amount of Ag in the alloy decreases. The amt. is not appreciably altered by tempering.

J. C. S.

**Chemical constants and critical data.** FR. A. HENGLEIN. *Z. anorg. allgem. Chem.* 114, 234-40 (1920).—The chem. const. is calcd. by the equation  $C = \lambda_0/4.571T$ , where  $\lambda = (\lambda_0 + AT - BT^2 - \dots)(1 - p/p_k)$  is the latent heat and  $p_k, T_k$  the crit. consts. Nernst's equation,  $C = 0.14\lambda/T_B$ , where  $T_B$  is the abs. boiling point, follows from van der Waals's equation,  $\log p/p_k = a(1 - T_k/T)$ . Cederberg's equation,  $C = k \log p_k$  (where  $k$  is 1.6 in many cases) also follows from this equation, since it is a special case of the more general equation,  $C = 1.1 \log p_k/(T_k/T_B - 1)$ . The formula  $\log p(\text{atm.}) = -2642/T + 2.5 \log T - 0.012175T + 8.474 \times 10^{-6}T^2 - 1.3325 \times 10^{-11}T^3 + 4.08355$  holds for water from 0° to the crit. point; for O the equation  $\log p(\text{atm.}) = -438.8/T + 2.5 \log T - 0.33752T + 1.223 \times 10^{-6}T^2 - 4.0085 \times 10^{-11}T^3 + 2.84387$  is deduced.

J. C. S.

**Application of statistics to chemical equilibria.** K. F. HERZFELD. *Physik Z.* 22, 186-91 (1921).—A report on the modern work in connection with the statistical method of treating chem. equilibria. The work is discussed in connection with the classical theory, the quantum hypothesis, and charged systems.

J. C. S.

**Vapor pressure of white phosphorus from 44° to 150°.** DUNCAN MACRAE AND C. C. VAN VOORHIS. Westinghouse Research Lab. *J. Am. Chem. Soc.* 43, 517-53 (1921).—The vapor pressure of liquid white P has been measured by the static isoteniscope method of Smith and Menzies. The results are expressed by the equation  $\log_{10} P_{(\text{mm. Hg.})} = 7.9512 - 2757.5/T$  to within 0.01 mm. Hg.

D. MACRAE

**Thermoelements. I. Thermal and electrical conductivities of copper-phosphorus alloys.** GEORG PFLEIDERER. *Ges. Abhandl. Kennt. Kohle* 4, 409-26 (1919).—The efficiency of the transformation of thermal into elec. energy by means of a thermoelement depends, not only on thermoelec. power, but also on the ratio of thermal to elec. cond.: the efficiency of the transformation will be less with increase of this ratio, which, according to the Wiedemann-Franz law, should remain const. Expts. on Cu-P alloys contg. 1.98 and 0.63% of P resp. failed to confirm previous observations of favorable variations in the ratio of thermal to elec. cond. It is concluded that there is no prospect of obtaining any increase in efficiency of thermoelements by modification of this ratio. II. The thermo-electric power of antimony-cadmium alloys of about 50 atomic percent. FRANZ FISCHER AND GEORG PFLEIDERER *Ibid* 440-7.—Sb-Cd alloys of approx. at. compn. show probably the highest thermoelec. power of all metals and alloys hitherto investigated. In one and the same fragment and in different fragments of the same alloy remarkably variable values for thermoelec. power were obtained, including some higher than any hitherto observed. Such variations suggest that the thermoelec. properties of this alloy are much influenced by inhomogeneity. The thermal treatment is also of importance in this connection. Thermo-elec. power is altered at higher temps., not only by a reversible temp. effect, but also by an irreversible alteration of the material. Amalgamation depresses thermoelec. power. Alloys prepd. by fusion under a mixt. of Li and Na chlorides showed particularly low values, which, however, were increased by subsequent heating without the covering of fused salts.

J. C. S.

**Compound formation and the electromotive behavior of cerium in its alloys with iron and zinc.** FRITZ CLOTOWSKI. *Z. anorg. allgem. Chem.* 114, 1-23 (1920).—C. has applied Dolezalek's theory of binary mixts. (*C. A.* 7, 2887) to the study of the binary alloys of Ce with Zn and Fe resp., and with its help has been able to demonstrate the presence of compds. in these alloys. For the prepn. of the alloys, pure Ce was not available, but



a metal was used contg. Ce metals 97.0% (Ce 92.5%), Fe 1.46%, Si 0.88%, C 0.35%. Ce-Fe alloys contg. from 3.9% to 84.1% of Ce, and Ce-Zr alloys contg. from 26.6% to 92.7% of Ce, were prepd., and the potential difference between the alloy and pure Ce was detd., in each case. It is shown on theoretical grounds that the concn.-potential difference curve in the case of a simple binary alloy, without compds., has a logarithmic form, but if a compd. is present in the alloy, a rapid increase of potential should take place at the concn. corresponding with the compn. of the compd. When more than one compd. is formed, the curve takes a horizontal course after the rise corresponding with the first compd., to rise again for the second compd. The curve for the Fe-Ce alloys indicates the existence of a compd., CeFe, and also of a second compd., CeFe<sub>2</sub>, but the compn. of the latter is to some extent uncertain. The Ce-Zn alloys show the presence of two compds., Ce<sub>2</sub>Zn and Ce<sub>3</sub>Zn. The velocity consts. of formation of the compds. were also calcd. with the help of the theory. The const. for CeFe is given as  $K = 10^{10}$  while for the Ce-Zn alloys the consts. are of the order  $K_{Ce_2Zn} = 4 \times 10^{17}$  and  $K_{Ce_3Zn} = 10^{17}$ .  
J. C. S.

**Electromotive behavior of aluminium-mercury alloys.** R. KREMANN AND R. MÜLLER. *Z. Metallkunde* 12, 289-303(1920).—Al amalgam was best prepd. using a soln. of HgCl<sub>2</sub>. The e. m. f. of cells of the type, Hg|0.1N KAl(SO<sub>4</sub>)<sub>2</sub>|Al<sub>2</sub>Hg<sub>2</sub>, was measured. The potential of Hg against the normal calomel electrode was +0.2, that of Al - 0.82 (const. values could not be obtained on account of the formation of surface layers), and that of the amalgam -1.314 to -1.352 volts, almost independent of the compn. The results indicate the formation of a compd. of Hg and Al, the compn. of which could not be detd. Similarly, in combinations of the type Hg|0.1N NaI in pyridine|Al<sub>2</sub>Hg, the potential of the amalgam is independent of its compn., about 0.25 volt less "noble" than that of Al.  
J. S. C. I.

**Electromotive behavior of magnesium-mercury alloys.** R. KREMANN AND R. MÜLLER. *Z. Metallkunde* 12, 303-12(1920).—The potential of pure Mg, as detd. from the combination, Pb|0.5 to 1.0N MgSO<sub>4</sub>|Mg, is -1.48 to -1.68 v. Slight amalgamation brings the value to -1.71 to -1.79 v. Mg and Hg readily combine at the b. p. of the latter. Mg amalgams when exposed to the air quickly become covered with a brownish black skin of MgO, Mg(OH)<sub>2</sub>, and MgCO<sub>3</sub>, colored with finely divided Hg; oxidation also occurs in a desiccator. Traces of Mg bring the potential of Hg to a value 0.3 volt less "noble" than that of Mg; this value persists up to 85 atoms % Mg, then rises a further 0.17 volt to a max. at 91 atoms % Mg, afterwards falling again. The max. may be due to a compd., Mg<sub>2</sub>Hg, less "noble" than either component, which is solid at ordinary temps. and forms mixed crystals with Mg and probably with Hg.  
J. S. C. I.

**Chlorine overvoltages.** EDGAR NEWBERRY. *J. Chem. Soc.* 119, 477-86(1921).—In keeping with the contention of the author that overvoltage cannot be accurately detd. without cutting off the charging current, contrary to the methods of American investigators, the Cl overvoltage is defined as the excess of back e. m. f. of an electrode above that of a standard Cl electrode in the same electrolyte. Results for a large no. of electrodes are given. Of these C, Rh, Ir and Pt are unattacked by anodic Cl; Au, Cr, Pd and Ti show passivity; Sb, Ta, W and Ti show valve action; Cu, Ag, Hg, and Pb are covered with an insulating coating; and Cd, Zn, Al, Sn, Bi, Mo, Mn, Fe, Co and Ni are dissolved. The results from a practical standpoint indicate that for moderate electrolytic chlorination, Pt electrodes, preferably platinized, with low current density are suitable whereas for powerful chlorinations waxed graphite electrodes are the only electrodes capable of giving the requisite high overvoltage. For a given element the Cl, H and OH overvoltages are remarkably similar, giving confirmation to the law that elements in the same group in the periodic system show the same overvoltages.



Graphite with a value of 0.18 v. persistently acts like an element in Group VIII, suggesting that the atom must contain a double nucleus with the outer valency electrons rotating around it. This capacity for the simple C nuclei to coalesce may account for the tendency to form long chains and for the abnormal behavior of the first member of homologous series. Thus Me and Et ales. would be resp.,  $\text{CH}_3\text{OH}$  and  $(\text{Gr})\text{H}_3\text{OH}$ . The following outstanding conclusions from all the work on overvoltage are drawn. (1). Overvoltage is produced only when gases under high pressure are liberated. (2) For any one electrode it is the same whatever gas is liberated. (3). The nature of the electrode surface, its material, the nature and soly. of the gas, current density and time are all factors in detg. the gas pressure set up and hence are a part in detg. the composition of compds. responsible for overvoltage. (4). Otherwise the overvoltage is independent of the element but dependent upon its valence, *i. e.*, the increment in single potential depends only upon the no. of loosely bound valency electrons. (5). *The single potentials of the elements are periodic functions of their at. nos.* G. L. CLARK

**Accurate measurement of the electrical conductivity of electrolytes at temperatures up to 1600°.** F. M. JAEGER AND B. KARMA. *Z. anorg. allgem. Chem.* **113**, 27-58 (1920).—The authors have described a method for the detn. of the elec. cond. of molten salts which may be used up to 1600°. An elec. tube furnace is employed for obtaining the required temp., which may be kept const. to 0.1°. Temp. measurements are made by means of a Pt Pt-Rh thermo-element, which is placed exactly in the center of the melted salt. The electrode vessel is a small Pt tube with a rounded bottom (35 mm. diam. and 10 mm. high), which is suspended in the tube furnace by 3 Pt wires 1.5 mm. diam. The crucible itself constitutes one electrode, and the other is a similar vessel of 10 mm. diam. The Pt used must be absolutely free from Ir. Full details are given for the detn. of the cell const., and all precautions necessary in the measurements are fully described. The following salts have been measured over the temp. range indicated, and the mol. cond. is given in tables, which are reduced to a general formula in each case, by means of which the mol. cond. may be calcd. for any temp.  $\text{KNO}_3$  (346.1-500.4°),  $\mu_t = 36.21 + 0.1875(t-350)$ ;  $\text{NaNO}_3$  (321.5-487.3°),  $\mu_t = 41.56 + 0.205(t-300)$ ;  $\text{LiNO}_3$  (272.0-440.6°),  $\mu_t = 41.14 - 0.238(t-300)$ ;  $\text{RbNO}_3$  (318.8-493°),  $\mu_t = 33.51 + 0.145(t-300)$ ;  $\text{CsNO}_3$  (446.6-556.3°),  $\mu_t = 12.13 + 0.120(t-450)$ ;  $\text{KF}$  (863.0-975°),  $\mu_t = 101.8 + 0.3163(t-900)$ ;  $\text{KCl}$  (775.7-943.5°),  $\mu_t = 115.4 + 0.2575(t-800)$ ;  $\text{KBr}$  (745.2-868.6°),  $\mu_t = 90.09 + 0.1906(t-750)$ ;  $\text{KI}$  (661.3-814°),  $\mu_t = 85.41 + 0.1501(t-700)$ ;  $\text{Na molybdate}$  (845-1408°),  $\mu_t = 107.59 + 0.1837(t-850)$ ;  $\text{Na tungstate}$  (752.5-1501°),  $\mu_t = 83.59 + 0.185(t-750)$ . The exptl. values are compared with those calcd. by the formulas, and in every case there is a good agreement J. C. S.

**The magnetizability of the rare earths.** E. WEDERKIND [with P. HAUSKNECHT]. *Ber.* **54B**, 253-8 1921 cf. *C. A.* **9**, 1268. The following values have been obtained for the at. magnetism,  $\gamma \times 10^{-6}$ , of a series of metals of the rare earths, the observations being made with spectroscopically pure specimens of the oxides, sulfates, and oxalates:

	Sc	Y	La	Ce <sup>III</sup>	Ce <sup>IV</sup>	Pr	Nd	Sm	Gd	Er
Oxide	-1.2	+8.7	-18.3	—	+74.1	+47.0	+5100	+8300	+9850	+40,600
Sulfate	-62.5	-57	-81	+2200	+37.5	+5100	+5270	—	—	+36,700
Oxalate	-65	—	—	—	—	+5000	+5380	—	+9430	+35,800

The values for Sc, Y, and La are too small to be regarded as trustworthy. If the values for the at. magnetism are plotted against at. wts. a graph is obtained which shows a flat max. at Y, and a second max. in the cerite group, either at Nd or Sm, according to the value adopted, the curve then descends to Eu and subsequently rises somewhat steeply but regularly through Gd and Th to a high max. at Dy, after which it falls steeply and evenly through Ho, Er, Yb, to lutetium. J. C. S.



**Piezoelectric analysis.** II. Investigation of systems of which the temperature of solidification can pass through a maximum. JEAN TIMMERMANS. *Bull. acad. roy. Belg.* 1919, 753-66; cf. *Ibid* 1913, 810-30.—T. discusses the form of piezometric curves for a pure substance the f. p. of which passes through a max. with increasing pressure. Similar considerations are applied to mixts. of substances of this type. III. Crystallization under increased pressure and its relationship to the mutual solubility of liquids. *Ibid* 767-85.—The process of solidification of systems consisting of two liquid layers under high pressure is investigated theoretically and illustrated by many piezochem. curves. The original must be consulted for details. J. C. S.

**Diamagnetism of monatomic gases.** W. PAULI, JR. *Z. Physik* 2, 201-5 (1920).—Debye (*C. A.* 15, 2226) has shown that van der Waal's  $a$  depends only on the dielec. const. of the gas and terms of the form  $\sum ex^2$  that are summed over the individual charges and are called the quadruple moments. P. deduces a relation between these moments and the magnetic susceptibility for monatomic gases, but considers that it would lead to values for these moments 10 times larger than any that could reasonably be expected for atoms whose dimension are around  $10^{-8}$  cm. F. C. HOYT

**Magnetization of gases, and the magneton; oxygen and nitric oxide.** E. BAUER AND A. PICCARD. *J. phys. radium* 1, 97-122 (1920); *Science Abstracts* 24A, 225.—The gases dealt with were the two paramagnetic gases, O and NO. The principle of the method was to measure, in turn, the change of level of water in a tube when subjected to a magnetic field in an atm. of H and then in the gas under test. H is so feebly diamagnetic that its magnetization is negligible, and the change of level in this gas is due simply to the repulsion of the water by the field. In a magnetic gas, the change of level measures the repulsion of the water added to the attraction of the gas. Two methods of measuring were employed: in the second, an O-tube was substituted for a U-tube; this enabled the expt. to be continued for a long time without changing the water. The fact thus emerged that the soln. of gas in the water causes an error, the susceptibility being always too small. The values obtained were: for O ( $107.8 \pm 0.3$ )  $10^{-6}$ , and for NO ( $48.7 \pm 0.25$ )  $10^{-6}$ . The numbers of magnetons, calcd. by the usual method, were 7.08 and 9.20 for O<sub>2</sub> and NO, resp. A theoretical discussion, based on the probable value of the moment of inertia of the O mol., leads to the conclusion that Reiche's theory of magnetism, founded on Planck's second hypothesis of quanta, appears to be in poor agreement with the results of Kamerlingh Onnes and his collaborators. (See also *C. A.* 13, 5.) H. G.

**Magneto-crystalline properties of Indian braunites.** K. S. RAO. *Proc. Indian Assoc. for Cultivation of Science* 6, Nos. 1 and 2, 87-91 (1920); *Science Abstracts* 24A, 227.—Braunite is a natural ore of Mn which occurs in great abundance in various parts of the country, and which is invariably slightly magnetic. Two specimens from Kacharwahi and Kandri were ground into spheres of respective densities 4.8 and 4.22. The av. intensity of magnetization was calcd. from the pull experienced by the specimen in the non-uniform field of a powerful electromagnet. The max. field used was about 4000 gauss and the susceptibility was  $0.4 \times 10^{-5}$ . The specimens have a magnetic axis of symmetry with a perpendicular plane in which the susceptibility is independent of orientation. Along the axis of symmetry the susceptibility is a minimum, and in the plane it is a max., the difference being about 2%.

**Point discharge in nitrogen.** M. PIRANI (with E. LAX). *Wiss. Veröffentl. Siemens-Konzern* 1, 167-78 (1920).—The investigations were undertaken with the object of elucidating a method for the detection and, if possible, estm. of minute traces of impurity, particularly of aq. vapor, in N and the rare gases. They are based on the observations of Franck and Hertz (*C. A.* 10, 3023), according to which an electron formed in the neighborhood of a point cathode in a pure gas can lead to a strong ionization, and consequent variation in the current, which, however, is irregular in occurrence,



owing to the infrequency of the phenomenon. On the other hand, the presence of minute amts. of electronegative substances, such as O, oxides of N, or water, causes an increase in the current, owing to the production of electrons at the cathode. Such a gaseous mixt., however, does not behave in a stable manner, the phenomena being complicated by the occurrence of slow chem. changes, which cause gradual alterations in the strength of the current, in accordance with the nature of the chem. processes. With a pure gas, the current rises initially, owing to the liberation of inherent impurities by the heat, but falls when the max. of impurity has been passed. In an impure gas, on the other hand, more strongly electronegative products (such as NO) may be readily formed, thus causing a decrease in the current, which subsequently rises after partial or complete absorption of the impurities by the electrodes. The app., which is operated in duplicate, consists of a 2-l. globe furnished with an Al plate and a Mo point as electrodes, the current being provided by an a. c. high-tension transformer. In spite of somewhat considerable individual variations, the same characteristics are exhibited by both sets of app. The electrodes need to be replaced frequently, as they are attacked by the impurities (O and aq. vapor). The pressure of the N is 700 mm. The sources of error are fully discussed, and it is shown that the differences due to beating effects are invariably smaller than those due to impurities. The pure N is obtained from the compressed gas by absorption of O and subsequent desiccation, the last traces of O and aq. vapor being removed by passage over finely divided Ta (which has been completely freed from gases) at 1000°. Such N, with a const. alternating tension of 4320 v., gave a current time curve which rises to a max. in the first 3 min., and sinks more or less pronouncedly subsequently.  $10^{-4}$  amp. may be regarded as mean value for the current in pure N. With this current, a dark space of a few tenths of a mm. surrounds the point enclosed by a violet band, from which pass brush discharges; if O is now admitted, the discharge shrinks progressively until it can only be observed with a lens. With increasing O content, the minimum current becomes progressively smaller, and the rise in the time-current curve occurs after a longer period. The max. current strength depends in some way on the O content. The time-current curves for mixts. contg. O, in contrast to those for pure N, exhibit a steep rise after a time. Obviously, the O is gradually consumed, possibly by formation of NO, which is removed by the Mo or other oxidizable part of the app.; such removal is not, however, quant., and minute traces of O remain, which raise the current strength above the normal value. The mixt. in which the greatest rise was observed contained about  $5 \times 10^{-4}$  %. Since measurements with similar vessels agree to within  $\pm 10\%$ , the O content can be measured (up to  $5 \times 10^{-3}$  %) after calibration of the app. with mixts. of known compn. In a similar, but less simple manner, the content of aq. vapor can be estd. The appearance of the point discharge is more considerably modified by water vapor than by O. The time-current curves, in contrast to those of mixts. contg. O, exhibit a definite and less defined minimum, which gradually disappears with increasing water-vapor content, and, in particular, shows a gradually rising branch, the current values for which with mixts. poor in aq. vapor lie above those for pure N, and appear to lead asymptotically to a final value. The processes on which these curves depend are obviously very complicated, owing to the dissoc. of water vapor. With slight modifications, the expts. can be extended to the rare gases; the sensitiveness is greater in these cases, but the phenomena are generally similar. The presence of H in N to the extent of 0.1% or more can be detected with certainty by means of the time-current curves, but the slight elasticity of the H mols. renders the method less sensitive. Apart from its analytical application, the method appears suitable for the investigation of the affinity of various substances at different temps. for aq. vapor, the dependence of the activity of reducing substances on temp. and state of division, and the after-glow of active N.

J. C. S.



The dielectric constants and the refractive indexes of fluids. HECTOR ISNARDI AND R. GANS. *Physik. Z.* 22, 230-3(1921).—Preliminary paper on the results obtained with  $\text{Et}_2\text{O}$  in an attempt to compare with the theory of Gans (*C. A.* 15, 2581) the variation of the dielec. const. of fluids with change in temp. The results favor the views of Gans rather than those of Debye (cf. *C. A.* 6, 1087). JEROME ALEXANDER

A new method for the production of undamped electromagnetic oscillations (NASARISCHWILY) 3. Formation of crystals by directed vapor molecules (GROSS, VOLMER) 3. The detection of parts of different "nobility" in a piece of metal (KYROPOULOS) 9.

ORTOLEVA, GIOVANNI: Nozioni di Chimica Generale per Istituti Tecnici. Milano: Libreria Editrice Giuseppe Tamburini, Piazza Mentana 3. For review see *Boll. chim. farm.* 60, 250(1921).

### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

Presentation of the Gibbs Medal to Mme. Curie. *Chem. Met. Eng.* 24, 1132-40 (1921). For chemistry. HERBERT N. MCCOY. *Ibid* 1132-5. For physics. R. A. MILLIKAN. *Ibid* 1135. For geology. T. C. CHAMBERLIN. *Ibid* 1135-6. For astronomy. E. B. FROST. *Ibid* 1136-7. For medicine. W. A. PUSEY. *Ibid* 1137. Presentation of the medal. JULIUS STIEGLITZ. *Ibid* 1137. Acceptance address. MME. CURIE. *Ibid* 1137-40. E. H.

Some dimensions of the atom. L. ST. C. BROUGHALL. *Phil. Mag.* [6] 41, 872-6 (1921).—If the at. diameter  $\sigma$  be calcd. from the van der Waals equation by the formula

$$\sigma = \frac{(3b)^{1/3}}{(2\pi N)} \text{ in which } N = \text{number of mols. per cc. at } 0^\circ \text{ and } 760 \text{ mm.} = 2.75 \times 10^{19},$$

and  $b$  is the van der Waals const., the values obtained for the diameters of the successive inert gases, He, Ne, Ar, Kr, Xe, differ from each other by a const. amt.,  $0.28 \times 10^{-8}$  cm. This const. difference is in accord with the Langmuir's law  $N(\text{at. number}) = 2(1^2 + 2^2 + 3^2 + \dots)$ . Assuming the position of the atoms as given by Langmuir and that the law of the inverse square of the distance holds for the elec. forces, B. shows how the attractive and repulsive forces may be calcd. on any electron of the lighter atoms. S. C. L.

The probable normal state of the helium atom. EDWIN C. KEMBLE. Harvard Univ. *Phil. Mag.* [6] 42, 123-33(1921).—K. discusses the arguments against the Franck and Reiche (*C. A.* 14, 2580) model of the He atom, and summarizes his conclusion as follows: The model of the normal He atom proposed by Franck and Reiche cannot be correct, for it gives no explanation of the chem. properties of He, it gives the wrong ionization potential, and does not harmonize with the observations of Fricke and Lyman on the ultraviolet emission spectrum of He. The exptl. facts regarding the excitation of the various lines in the arc spectrum of He show that the only stationary states from which direct passage to the normal state is ordinarily possible are those of the series (m, S); that the direct transfer of atoms from the states (m, S) to the normal takes place with relative difficulty; and that the presence of some common impurity in He provides an indirect path for the return of atoms to the normal state, which is accompanied by the emission of more than one radiation frequency. The application of the Bohr principle of selection to the passage of atoms from the stationary states of higher energy to the normal state, if legitimate, leads to the conclusion that the resultant angular momentum of the normal He atom is zero. Neither of the two possible models



having zero angular momentum is very satisfactory, and it seems probable that the application of the Bohr principle of selection to atoms returning to the normal state will have to be abandoned. A symmetrical model with one unit of angular momentum, similar in many respects to that of Franck and Reiche, is suggested as a possible solution of the problem.

S. C. LIND

**Magnetism and the constitution of atoms.** PIERRE WEISS. *Rev. sci.* **58**, 645-59 (1920).—In this lecture Weiss reviews his work on magnetism with especial reference to his idea of the existence of a unit of magnetism and molecular magnetic fields. The atomic magnetic moment of iron divided by 11 gives 1123.6; that of nickel divided by 3 gives 1123.3. This suggests that the atomic magnetic moment of a substance may be expressed as an integral multiple of a more elementary magnetic moment than that found in the atom. Hence the hypothesis of a fundamental magnetic moment out of which all atomic magnetic moments can be built up as whole multiples. This unit is called the magneton. It is thought of as forming one of the constituents of atoms in a way similar to the way in which electrons enter into them. The evidence for the existence of the magneton is deduced from a study of the susceptibility of alloys and compounds of magnetic metals. The number of magnetons in a series of nickel-cobalt alloys is an additive property. The number of magnetons in a series of nickel-iron alloys is represented by two straight lines intersecting at the concentration corresponding to the compound  $\text{Fe}_3\text{Ni}$ . There are 10 magnetons in the compound  $\text{Fe}_3\text{Ni}$ —a value intermediate between 11 in iron and 3 in nickel. A similar study of cobalt-iron alloys shows that in the compound  $\text{Fe}_2\text{Co}$  there are 12 magnetons—a number in excess of 11 in iron or 9 in cobalt. This result is difficult for the theory, since the number of magnetons seems to have been increased by alloying. A study of nickel chloride, nickel sulfate and nickel nitrate indicates that there are 16 magnetons in each atom of nickel, whatever the concentration of the salt. When  $\text{FeCl}_3$  is in dilute solution there are 27 magnetons and in concentrated solution there are 20 magnetons. This variation indicates that an ion of iron has 27 magnetons and that a neutral molecule has 20 magnetons. The fact that the addition of  $\text{HCl}$  to a dilute solution of  $\text{FeCl}_3$  decreases the degree of dissociation and at the same time increases the number of magnetons seems to show the correctness of this explanation. In a similar way the atomic magnetic moment of iron in iron-sulfate and of cobalt in cobalt-sulfate increases with the concentration of the salt. This increase may arise from a decrease in the degree of dissociation. Vanadium sulfate, which has been studied by Ercluisse, suggests that vanadium has 8 magnetons in one condition and 9 magnetons in another condition. The importance of the magneton in the description of the atom is pointed out. The atom of iron may have 10, 11, 12, 26, 27 or 29 magnetons. The atom of nickel may have 3, 8, 9 or 16 magnetons. The magneton is important in determining the chemical union of atoms and in fixing other chemical and physical properties. The molecular field is important in explaining such phenomena as cohesion, pyroelectricity and piezoelectricity.

A. W. SMITH

**The possibility of separating mercury into its isotopic forms by centrifuging.** J. H. J. POOLE. Iveyagh Geol. Lab. *Phil. Mag.* [6] **41**, 818-22 (1921).—A mathematical treatment of the possibility of separating the isotopes of liquid Hg is dealt with on the assumption of only two principal components differing in at. wt. by 4 units, and that the at. vols. are identical. The case is first considered for a column in equilibrium under the force of gravity and then under centrifugal force such as would be produced in the apparatus already described (*C. A.* **14**, 1127). It is calculated that the difference produced at the two ends of the centrifuge would be only 1 part in 30,000, which would hardly be possible to detect with certainty.

S. C. LIND

**Different kinds of radioactive disintegration and the possibility of their explanation**



on the basis of nuclear structure theories. LISE MEITNER. *Z. Physik* 5, 146-56 (1921).—Modern theories indicate the following structure for a nucleus of at. wt.  $A = 4n + p$ , ( $p = 0, 1, 2, 3$ ) and at. number  $z$ . There are  $n$  He nuclei and  $pH$  nuclei. If  $z$  is even there are  $z/2$  He nuclei with a double positive charge and  $n-(z/2)$  whose charge is completely neutralized by two electrons. All the H nuclei are neutralized. If  $z$  is odd there is a free electron present. Calling charged He, neutral He, and free electrons  $\alpha$ ,  $\alpha'$ , and  $\beta$ , respectively, M. classifies radioactive transformations into four kinds: (1) a series of successive  $\alpha$ -transformations,  $\alpha - \alpha - \alpha$  (2) an  $\alpha'$ -transformation

followed by two  $\beta$ -transformations, (3) a transformation of the form  $\beta - \alpha' - \alpha$ , where

two different processes give the same end product, and (4) a splitting into two independent series by  $\begin{matrix} \alpha & & \alpha \\ & \searrow & \swarrow \\ & \alpha' & \beta \end{matrix}$  or  $\begin{matrix} \alpha & & \alpha \\ & \swarrow & \searrow \\ & \alpha' & \beta \end{matrix}$ . M. shows how all known transformations can be thus

classified.

F. C. HOYT

Isotopes and Gibbs' paradox. ERWIN SCHRÖDINGER. *Z. Physik* 5, 163-6(1921).—S. describes a method for the reversible mixing of two gases chemically inert to each other and differing only in mol. weight. It requires only a uniform gravitational field.

F. C. HOYT

Researches on the radioactivity of surface air. P. B. HUBER. *Arch. sci. phys. nat.* [5] 2, 508-10(1920).—P. Otujic has examined the emanations from clayey soil and has found that the ionization near the surface is much less when the soil is damp than when it is dry, also when it is compact than when it is broken up, and further that it is almost nil over snow. H. has conducted similar expts. over gravel, and finds confirmation of the above in that greater ionization accompanies dry soil than wet and so on, but the percentage differences are not the same as for a clay soil. Besides, the abs. values appear higher over gravel. These results were obtained with app. consisting of a cylindrical sheet-iron receiver 30 cm. wide and high, open at the base and with a hole of diam. about 8 cm. at the top. A plate, 15 cm. in diam. and 15 cm. from the ground, was connected through this hole with an electrometer above. The expts. were made between 1:30 and 2:15 p.m. It is known that during the foehn the ionization of the air is above normal. The present expts. show that this is not due solely to the descent of strongly ionized air from higher levels, but that at the same time the emanations from the surface are above normal. Other cases of strong ionization are mentioned, which on investigation proved to be confined to a layer 20 to 30 m. above the surface, the ionization at 50 m. being normal. This condition is observed to precede a change of weather.

H. C.

The fluctuations of alpha radiation. MILLE. A. MUSZKAT and L. WERTENSTEIN. Warsaw. *J. phys. radium* 2, 119-28(1921).—M. and W. point out that in spite of the exptl. verifications of the v. Schweidler theory (Internat. Congress Radiol. Liege, 1905) by various authorities the results are illusory. This is partly due to the incorrect data earlier employed and to the use of non-homogeneous  $\alpha$ -radiation, as well as neglect of proper consideration of the factors involved in the electrometric detns. M. and W. have developed a theory with great elaboration which they apply to the fluctuations of  $\alpha$ -radiation from Po. The agreement between theory and observed number for 304 fluctuations is satisfactory.

S. C. LIND

The general law of errors, the fluctuation of the field strength in a dielectric and the scattering of  $\alpha$ -rays. W. BORNE. Charlottenburg. *Z. Physik* 5, 63-9(1921); cf. *C. A.* 15, 2240.—B. derives the general law of distribution of errors for a given



number of independent sources of error and applies it to the above phenomena. In the first case the distribution law is a simple one, different from that of Gauss, and in the case of the scattering of  $\alpha$ -rays there are two series of additional terms in addition to the Gauss law which holds to a first approximation.

F. C. HOVR

The Einstein gravitational displacement in the case of the nitrogen band  $\lambda = 3883 \text{ \AA.}$  in the sun's spectrum. L. GREBE AND A. BACHEM. *Z. Physik* 2, 415-22 (1920).—The absence of pressure and pole effects in the case of the N band  $\lambda = 3883 \text{ \AA.}$  makes this band suitable for the investigation of a possible Einstein gravitational effect on the sun's spectrum. The authors, by a microphotometric comparison of the cyanogen band emission spectrum with the sun's absorption spectrum, conclude that only 9 of the 36 cyanogen lines previously measured are sufficiently free from objection to be used in the present connection. Employing these 9 lines only, the authors obtain the mean value  $0.56 \text{ km. per sec.}$  as the displacement, compared with the values  $0.63 \text{ km. per sec.}$  deduced from Schwarzschild's observations,  $0.67 \text{ km. per sec.}$  deduced from the observations of Evershed and Royds, and the value of  $0.32 \text{ km. per sec.}$  given by St. John's results, in each case employing only such of the observed lines as are included in the nine free from objection. The authors conclude that the displacement predicted by Einstein is correct, both in magnitude and direction.

J. C. S.

Light and electrons. OLIVER LODGE. *Phil. Mag.* [6] 42, 177-83 (1921).—A speculative paper dealing with the liberation of electrons by light. It is assumed that when under light stimulus, or otherwise, an electron is liberated from complete neutrality or "practical nonentity" that the opposite charges may be thought of as initially united by an elastic thread of zero length gradually elongated till it snaps and that soon afterwards the ordinary law of inverse square applies. When the particle flies away the energy of escape is half the energy from infinity under an inverse square law. Expressions are deduced for the critical velocity, critical distance and critical frequency. The critical distance is  $\frac{0.53}{10^{15} N} \text{ cm.}$  in which  $N$  is the at. number, so that the break occurs inside the conventional atom at about  $1/2$  the radius for H and about  $r/40$  for the heaviest atoms. The critical frequency most suitable for expelling an electron from an atom is

$\pi = \frac{6.4}{1.56} \times 10^{16} \times \frac{N^2}{2\pi}$  which is  $6.53 \times 10^{13}$  for H, increasing with  $N^2$  to  $5.5 \times 10^{14}$  for U. The critical velocity of expulsion is  $v = \frac{2.53}{1.16} \times 10^8 N$ , which for H is  $2.18 \times 10^8$  and reaches  $2/3$  the velocity of light for U. In a note on at. instability it is shown that the electronic velocity attained by random impulses would be short of the critical value for escape by  $26 N$ . Taking into account the factor  $1 - (v^2/c^2)$ , which is effective in reducing the holding force, the unaided gas speed for ordinary temps. is insignificant, but as the critical velocity is approached  $1 - (v^2/c^2)$  can become 0.55 for U and 0.64 for Pb. The temp. at which electrons should be liberated without any sp. radiation stimulus is calcd. to be  $T = 2 \times 10^7 N^2$ , an appallingly high temp. In the presence of synchronous radiation the temp. might be lowered to within the locally high temp. of the sun of  $7100^\circ$ , when electrons would be liberated at  $1/140$  the speed of light, which would pass the earth in about 18 hours.

S. C. LIND

Recent results of northlight investigations and the nature of the cosmic electric rays. L. VEGARD. Univ. of Christiania. *Phil. Mag.* [6] 42, 47-87 (1921).—A very exhaustive discussion of the probable nature of the rays causing the aurora polaris. The phenomena are described in detail, and tables are presented showing the height measurements made at various times and places for rays, draperies, drapery-shaped arcs, diffuse arcs, and pulsating aurorae. The latter have been observed at a height as low as  $73 \text{ km.}$ ; rays have not been observed below  $93 \text{ km.}$ ; the greatest density of illumination from all sources is in the region  $100$  to  $105 \text{ km.}$  No observations have



been made above 157 km. The shape of the arcs is also fully discussed as having a bearing on the question. While no perfectly definite conclusion is reached, V. favors the view that the rays are either of the nature  $\alpha$ -rays, or canal rays, or else are electronic in nature. The penetration of an H particle into the upper atm. would under certain plausible assumptions, bring it within just about 100 km. of the earth's surface before it would be completely absorbed which would account for the lower limit of the aurorae. Other evidence favors the electronic nature of the stream. The change of color of the aurorae, which is sometimes very striking, is discussed; it is considered more probable that the change is due to a change in the velocity of the stream than to a change in the absorbing atm.

S. C. LIND

Dissociation of hydrogen and nitrogen by electron impacts. A. L. HUGHES. Queen's Univ., Kingston, Canada. *Phil. Mag.* [6] 41, 778-98(1921).—H. summarizes his results as follows: The disappearance of  $H_2$  and  $N_2$  at low pressures when an electron stream is passed through them has been investigated. For  $H_2$ , no disappearance was obtained unless the electrons had energy above 13 v. The rate of disappearance rose rapidly as the energy of the electron was increased to about 70 v., after which no rapid change was noted (the rate appeared to diminish somewhat when the energy of the electrons was raised from 150 to 300 v.). For  $N_2$ , the rate of disappearance was at first much less than for  $H_2$ , but when the energy of the electrons was raised sufficiently (roughly 200 v.) the rate of disappearance of the  $N_2$  exceeded that for  $H_2$ . Reasons are given for believing that this disappearance is due to the splitting of the mols., and that these atoms condense on the adjacent surfaces particularly if they are cold. The max. rate of disappearance of  $H_2$  occurred when electrons of energy corresponding to 140 v. were used. About one mol. disappeared for every six collisions. Langmuir's work on the thermal dissociation of  $H_2$  showed that the clean up, even under the most favorable circumstances, accounted for only  $1/7$  of the amt. of dissociation. Hence it is possible that when the electrons have the right amt. of energy a dissociation may occur almost at every collision. A peculiar clean up, apparently due to absorption of  $N_2$  by a platinum filament covered with BaO and SrO when cooled to the temp. of liquid air, was noticed.

S. C. LIND

The disappearance of gas in the electric discharge. II. N. R. CAMPBELL, *et al.* *Phil. Mag.* [6] 41, 685-707(1921).—A continuation of the work reported in Part I (*C. A.* 15, 466) in which the disappearance under elec. discharge of  $H_2$ , CO,  $N_2$ , A, both in the absence and presence of P is treated. In the presence of incandescent W,  $H_2$  disappears without the passage of discharge, as discovered by Langmuir. The gas disappearing adheres without change to the surface of the glass, especially to the cooler parts. When discharge is passed, the rate of disappearance of  $H_2$  is not greatly changed, but is complicated by the simultaneous liberation of absorbed gas by bombardment and by the appearance of  $H_2O$  vapor. In the discharge CO is converted into  $CO_2$ ;  $CO_2$  as well as CO adheres to the glass walls and can be liberated by heating. The quantity of  $CO_2$  which will adhere is very much greater than that of  $H_2$  which will also adhere.  $N_2$  disappears under the discharge but cannot be liberated again by heating the evacuated vessel. At the same time the filament wastes and the walls are blackened. It is probable that Langmuir's nitride  $WN_2$  is formed, but part of the gas is probably held in its original form by a covering layer of W. A disappears like  $N_2$  with much blackening of the bulb, but can be restored by baking, together with some  $H_2$  produced by bombardment of the glass. Hg has not been proved to disappear. The discharge through the vapor liberates large quantities of gas from the glass even when previously baked in high vacuum. It is concluded that all gases can be made to adhere to glass by discharge in such a way that part, at least, can be liberated by baking, the amt. depending on the nature of gas and glass. The adhesion is not primarily chem., although chem. action



may result in a more easily adhering gas. Discharge can also liberate gas from the walls, doubtless by ionic bombardment, and some of the gas so liberated cannot be liberated by heating to the softening point of glass. The limit of absorption is reached when it is equaled by the release by bombardment. The action of P is treated fully, and the conclusion reached that its effect in removing gases is physical not chem. Yellow P vapor is converted into red P, which deposits on the walls, probably covering the deposited gas and thus preventing its liberation by bombardment. At the same time it provides a new surface on which further gas can be absorbed. S. C. LINN

Nature of ions produced in air by radioactive-bodies; ions of high mobility. J. J. NOLAN. *Proc. Roy. Irish Acad.* 35, 38-45(1920); *Science Abstracts* 24A, 200-1.—In an examn. of the ionization produced by spraying water, N. obtained evidence of the existence of a great variety of ions, some of them of much greater mobility than that ordinarily attributed to the small ion in air. A more complete examn. revealed that several groups of such mobile ions existed, some of very high mobility. In addition, a number of other groups were sep'd. out, the mobilities of which roughly corresponded with those observed for ions produced in air by the ordinary ionizing radiations. Four such groups were especially noted. These groups contained ions having for mobility in unit field (volt/cm.) the values 1.91, 1.70, 1.49, and 1.34 cm./sec. resp. It was suggested by N. (1) that all these ions consist of clusters of water-mols. of different sizes, the very mobile ions corresponding to the very small groups (one, two, three mols., etc.), and the others, such as the 4 mentioned above, consisting of larger groups of regularly graduated size; (2) that the ordinary small ion in air and other gases is also a stable cluster of water-mols., identical with one or other of the 4 forms mentioned above, the particular form prevailing at any time depending on the sign of the charges, and also on the degree of humidity. Using radioactive sources of ionization, N. has since repeated his observations of mobilities by the same method as that devised for the measurement of mobility of spray-ions. The results of these observations show conclusively (1) that when ionization is produced in moist air by radioactive substances the bulk of the ionization is carried by ions of 4 distinct classes, having mobilities 2.0, 1.78, 1.56, and 1.40 approx.; (2) that among negative ions the two faster groups tend to predominate, while among positive ions the slowest kind carries a large part of the ionization; (3) that, in addition, ions of mobility up to 12.5 are present in distinct groups, but in small quantities. H. G.

Radioactive constants according to the position in 1920. STEFAN MEYER. *Jahrb. Radioakt. Elektronik* 17, 80-7(1920).—Tables of consts. deduced from the most trustworthy data are given for the various families of radioactive elements. The tables include the half life, disintegration const., the av. life, the initial velocity of the corpuscles, the absorption coeff. of Al and Pb, and the range of the particles. J. C. S.

Volatilization of thorium B and thorium C deposited on gold. STANISLAW LORIA. *Krakauer Anzeiger* 1917, 260-4.—The volatilization of a radioactive product deposited on metal was examd. in the case of Th B+Th C deposited on Au. The volatilization of Th B from Au begins sooner than from Pt and Pd and throughout the temp. interval 300-1000° is greater from Au than from the other two metals. The volatilization of Th C from Au is very similar to that from Pt. In both cases there occurs a discontinuity on the volatilization curve at about 760°, which may be referred to the occurrence of Th C oxide, stable in this region of temp. This discontinuity is not shown for Th C on Pd. J. C. S.

Relative ionization of different gases by  $\alpha$ -rays. VIKTOR F. HESS AND MARIA HORNYAK. *Wien. Anzeiger* 1920, 219.—Measurements were made of the total ionization by  $\alpha$ -rays from Po of CO<sub>2</sub>, N, O, H, and coal gas compared with that of air. For CO<sub>2</sub>, using the full range of the radiation, it was about 23% greater and for coal gas



about 12% less than for air. By restricting the range of the radiation used, that is by using  $\alpha$ -rays of smaller velocity, quite different relative values were obtained, from which it is concluded that the form of the Bragg curve is notably different for the different gases, particularly in the terminal portion of the range. For example, using the last 3 mm. of the range, the ionization for  $\text{CO}_2$  was 8% smaller, for coal gas 22% smaller, but for H 25% greater than for air.

J. C. S.

**Critical electron velocities for the production of luminosity in atmospheric neon.** FRANK HORTON AND ANN CATHERINE DAVIES. Univ. of London. *Phil. Mag.* [6] 41, 921-40 (1921); cf. *C. A.* 15, 336, 1854.—Further expts. have been made (cf. *C. A.* 14, 1482) with Ne of higher purity to try to det. the critical voltages at which radiation of different types is produced in Ne. Several current-voltage curves are given indicating breaks at which sudden increases of current occur with increasing voltage. The conclusion is reached that there is no luminosity produced in Ne at 18.7 v. as earlier reported; the corresponding spectral lines probably belong to the invisible region. The lines produced first at 20 v. belong to the principal series (1.5  $s-m$ ,  $p$ ), while those at 22.8 v. are all of the (2  $p-m$ ,  $s$ ) and (2  $p-m$ ,  $d$ ) types, subordinate series. The possibility of the different isotopes of Ne being excited to radiation at different voltages is considered. The results cannot be simply interpreted in the light of the Lewis-Langmuir at. structure.

S. C. LIND

**Note on the question of the elementary electric quantum.** ERICH SCHMID. Vienna. *Z. Physik* 5, 27-30 (1921).—S. makes an experimental comparison between the two methods of calcg. the charge on an electron, the law of falling and the Brownian movement. Values of  $N$  are computed from the equation  $Nmg = 2RTv/\lambda$ , with the assumption of the Knudsen-Weber law of falling to find  $mg$ .  $\lambda^{-2}$  is the mean square of the Brownian displacement computed from several hundred observations on Se particles, and  $v$  is the velocity of fall under gravity. The results are in agreement with accepted values for  $N$ . They also seem to agree with those computed from the law of falling in the usual way. Individual detns. seem to group themselves around three different values, and S. suggests that the density of the particles may not be an absolute const.

F. C. HOYT

**Electron impact and the stratified discharge.** WALTER GROTRIAN. *Z. Physik* 5, 148-58 (1921).—Quantum relations in the inelastic impact of electrons serve to explain the appearance of strata in a Hg discharge tube. The accelerated electrons from the filament produce resonance radiation ( $\lambda = 2536 \text{ \AA.}$ ) when their velocity reaches that corresponding to about 4.9 volts for a multiple of this. As their velocity increases from the filament to the anode a series of bright bands is thus produced. The number of strata at a given voltage then serves to det. the critical potential of this line and G. gets a value  $4.90 \text{ \AA.}$  in good agreement with direct detns. A series of emission bands between 2349 and 2317  $\text{\AA.}$  is found in the positive column of a quartz Hg discharge tube, corresponding to a known absorption spectrum.

F. C. HOYT

**Excitation of the atom to light emission by electron impact. II. Spectroscopic studies of the neon "glow-discharge lamp."** R. SEELIGER AND G. MIERDEL. Greifswald. *Z. Physik* 5, 182-87 (1921); cf. *C. A.* 14, 3361.—This lamp (cf. *C. A.* 13, 286 for description) makes use of cathode glow in a mixt. of Ne, He, Ar and Hg. The change in intensity of individual lines with distance from the cathode is measured photographically. The lines reach their maxima at different distances, those with greater resonance potentials (where these are known) farther away in accordance with previous observations (*C. A.* 14, 2130, 3361). The intensity distribution among the lines of a series is different from that in the positive column.

F. C. HOYT

**Equilibrium conditions for electron emission from glowing bodies.** M. v. LAUS. *Jahrb. draht. Tele.* 16, 199-218 (1920); *Science Abstracts* 24A, 291.—The differential



equation for the steady state is first obtained and solutions are given for the cases of (1) a plane anode with a plane incandescent cathode; (2) an incandescent cylinder with an axially symmetric elec. field. The discussion is based on static considerations. (Cf. *C. A.* 13, 3070; 14, 3189.) H. G.

The effect of an electric current on the photoelectric effect. ALLEN G. SHENSTONE. Princeton Univ. *Phil. Mag.* [6] 41, 916-21 (1921).—S. has discovered that the passage of low current through a Bi plate increases the photoelec. effect to a marked degree. For a given plate current the photoelec. effect increases up to a max., which could be exceeded only by further increasing the current. With very high currents the max. was followed by a fairly rapid decrease in the photoelec. effect. In some cases two hours were required for attaining the max. On shutting off the current the photoelec. effect decreased at first rapidly, then more slowly, never reaching the original zero. Two theories of explanation are considered (1) a temp. effect, which is regarded as improbable on account of the low temp. coeff. of the photoelec. effect in general, (2) a change in orientation of the crystals more favorable to liberation of electrons. Sputtered plates of different thicknesses were tried successfully. S. C. LINO

Photoelectric conductivity of zinc blend. B. GUDDEN AND R. POHL. Göttingen. *Z. Physik* 5, 176-81 (1921); cf. *C. A.* 14, 3363; 15, 1856.—G. and P. find that the photoelectric sensitivity of ZnS decreases with the increased absorption owing to impurities (mostly iron) and conclude that the energy absorbed is the direct cause of the cond. The spectral distribution of the sensitivity proves to be the same whether the exciting light is perpendicular or parallel to the electric field. The change in the selective maximum with field strength previously observed is a secondary effect and due to the fact that small crystal particles were used and the effect of surface contacts masked other effects. With large crystals it is independent of field strength. F. C. HOYT

Photoelectric effect in audion bulbs of the oxide-coated filament type. T. W. CASE. *Trans. Am. Electrochem. Soc.* 39, preprint (1921); *Phys Rev.* 17, 398-40 (1921).—In investigating the photoelectric emission from the oxide-coated Pt filaments of high-vacuum Western Electric audion bulbs, an increased photoelectric effect was observed when the Ni plate was made negative. This is ascribed to the presence of a deposit of Ba or Sr metal on the Ni plate. The conditions for obtaining such a deposit are, an extremely high vacuum, the proper temp. of the oxide coated filament, and a certain electric field intensity between the filament and plate, which may be alternating and which is the same for BaO, SrO, and CaO. If the field intensity be increased no coating occurs. To deposit the Ba and Sr, a bright orange and a white-hot filament temp., resp., are necessary. Only minute quantities of Ca were deposited when a 20% Ir-Pt filament is heated as bright as it will stand for a few minutes. For the cells constructed the current in av. sunlight is approx. 100 to 150 microamps. Ba cells have a satn. voltage from 25 to 125 v. For Sr cells 170 v. is sufficient. (A high-vacuum Sr photoelectric cell is described in Bulletin No. 3 of the Case Research Laboratory, Auburn, N. Y.—Abstr.) D. MACRAE

Determination of the permeability of paramagnetic substances with the Wheatstone bridge. G. BOLCKENBERG. *Z. Physik* 5, 70-6 (1921).—E. employs the method of Heydweiller (Boltzmann Festschrift p. 4, 1903) with some improvements. For  $Mn(NO_3)_2$ ,  $CoCl_2$ ,  $NiCl_2$ ,  $CoBr_2$ ,  $FeSO_4$ , and  $FeCl_3$  the results are independent of the concn. in accordance with Wiedemann's law, to within the limit of error (0.5%), except for  $FeCl_3$ . Change of frequency from 1000 to 12,000 is without effect except in the case of the iron salts. F. C. HOYT

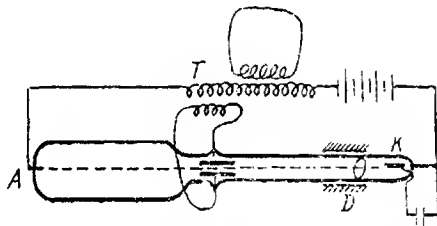
Paramagnetism of solid bodies. P. EISENFEST. Leiden. *Z. Physik* 5, 35-8 (1921).—E. derives the Curie-Langevin Law for the susceptibility of solid paramagnetic



substances on the following assumptions. The electrons rotate in orbits that are practically fixed in position and of the lowest quantum number. In the presence of an external magnetic field there is no noticeable difference in energy between the two opposite directions of rotation. For a given field and temp. there is a definite statistical equilibrium between these two directions of rotation.

F. C. HOVR

A new method for the production of undamped electromagnetic oscillations, which consists of the application of the electrostatic and magnetic properties of cathode rays for the rapid interruption of the current. AL. NASARISCHWILY. *Ann. Physik* 64, 759-60(1921).—A Braun tube (see fig.) has at *K* a hot cathode of the form described by Sampson. (*Ann. Phys.* 55, 610(1918)). An anode *A* is at the opposite end of the tube, where the fluorescent screen is ordinarily located. The coil *D* helps to focus the stream of electrons on *A*. The negative terminal of a battery of from 1800 to 3500 volts is connected to the cathode and the positive terminal to the anode through the primary windings of a transformer *T*. The terminals of the secondary windings are connected either to the plates of the condenser which produces the electrostatic deflec-



tions or to coils of wire which give the magnetic deflections. When the cathode is hot a current of from 0.9 to 9.7 milliamperes passes through the tube. While this current is being set up it produces an induced electromotive force in the secondary windings of the transformer. In either type of connection this causes a deflection of the stream of electrons,—in one case an electrostatic deflection and in the other case a magnetic deflection. This deflection of the cathode rays interrupts the primary current. With the interruption of the current the cause of the deflection of the cathode rays disappears and they again arrive at the anode. This reestablishes the primary current and the process continues as before. In this way high frequency oscillations are produced in the secondary of the transformer and in any neighboring circuit.

A. W. SMITH

The temperature coefficient of electric double refraction in liquids. C. BERGHOLM. *Ann. Physik* 65, 128-42(1921).—In an earlier investigation (*C. A.* 11, 2557) the author found that within a restricted interval of temp. the temp. coeff. of elec. double refraction in  $\text{CS}_2$ , *m*-xylene and bromobenzene agreed approx. with the value calc'd. from the theory of Langevin. In order further to test this theory it is necessary to extend the observations to a greater number of liquids and to make observations over larger intervals of temp. In the present investigation ten liquids have been studied,—toluene, *m*-xylene, chlorobenzene, bromobenzene,  $\text{CS}_2$ , chloroform, ethyl ether, ethyl bromide, benzene and  $\text{CCl}_4$ . Quant. results for the first 7 of the liquids are given. For many of the liquids used in this investigation the dependence of the dielec. const. on the temp. was unknown. Where necessary, measurements on the variation of the dielec. const. with the temp. were made by the method of Nernst. The other values as well as the values of the  $d$  and the index of refraction were obtained from the literature. If  $T$  is the abs. temp.,  $E$  the dielec. const. at  $t^\circ$ ,  $n$  the index of refraction at  $t^\circ$ ,  $\delta$  the  $d$  at  $t^\circ$ ,  $B_1$  = the Kerr const. at  $t^\circ$ .  $R = B_1 n^2 B_2 (K + 2)^2 (n^2 + 2)^2$ .



The observations on toluene, *m*-xylene, chlorobenzene, bromobenzene and  $\text{CS}_2$  show that  $R$  increases and the Kerr const. decreases with rising temp. In  $\text{CHCl}_3$  and  $\text{Et}_2\text{O}$   $R$  decreases with rising temp. and the Kerr const., which is negative, also decreases with increasing temp. The dependence of the Kerr const. on the temp. for different wave lengths of light was studied in toluene and  $\text{CS}_2$ . The variation of the Kerr const. with the temp. is nearly independent of the wave length of the light. Whether this is true in liquids in which the Kerr const. is negative it is impossible to say. In liquids in which the Kerr const. is positive  $R$  increases with rising temp. In liquids in which the Kerr const. is negative  $R$  also is negative and decreases with rising temp. Since in such liquids the numerical value of  $R$  decreases it is possible to say that in all liquids the value of  $R$  increases with rising temp. Assuming that double refraction is caused by the orientation of unsymmetrical mols. by the electric field, it is evident that the heat motions of the mols. must oppose such an orientation and consequently the temp. coeff. of all liquids should be negative. On the assumption that the dissymmetry of the mols. is independent of the temp. Langevin found  $R$  to be independent of the temp. Born introduces the idea of electric doublets to explain electric double refraction and finds that  $R$  must decrease with increasing temp. This is true for two of the liquids studied. Neither of these conclusions is in satisfactory agreement with the results of this investigation.

A. W. SMITH

The degradation of gamma-ray energy. ARTHUR H. COMPTON. Wash. Univ. *Phil. Mag.* [6] 41, 749-69 (1921).—C. summarizes the principal results of the investigation as follows: By far the greater part of the secondary gamma radiation from matter traversed by the hard gamma rays from radium C is fluorescent in nature. If any truly scattered radiation is present, at  $45^\circ$  it probably amts. to less than 15%, and for angles greater than  $90^\circ$  to less than 3% of the secondary rays. At large angles with the primary beam the scattered energy is probably less than 0.001 of that required by the usual electron theory. The secondary fluorescent radiation is found, in accord with observations by others on the whole secondary radiation, to be harder and more intense at small angles with the incident beam than at large angles, and tables are given showing the manner of this variation. While at large angles the radiation from heavy elements is somewhat more penetrating than that from the light elements, at small angles both the hardness and the intensity of the fluorescent radiation are approx. the same from elements covering a wide range of at. numbers. A study of the absorption coeffs. of this radiation in various elements shows that the softest parts of it, though of shorter wave length than the K-radiation from lead, are not harder than the most penetrating X-rays. The hardest parts approach in penetrating power the primary gamma rays from radium C. It is pointed out that the very small scattering observed is not incompatible with the classical electrodynamics, if the wave length of the gamma rays and the diameter of the electron are of the same order of magnitude. A satisfactory qual. explanation of the observed fluorescent radiation is found in the gamma rays produced by the impact of the secondary beta particles liberated in the radiator by the primary gamma rays. The observed asymmetry in the intensity and hardness may be accounted for if the oscillators which give rise to the fluorescent radiation are electrons moving in the direction of the primary beam with about half the speed of light. The wave length of the softest part of the observed fluorescent radiation is shown to lie between 0.06 and 0.12 Å. U., probably nearer the former value, while the wave length of the hardest part is probably about half as great. By a comparison of absorption coeffs., the effective wave length of the hard gamma rays from radium is estd. as about  $2$  or  $3 \times 10^{-10}$  cm.

S. C. LIND

**X-ray spectra.** W. H. BRAGG. *Proc. Phys. Soc. (London)*, 33, 1-12 (1920); *Science Abstracts* 24A, 194 Discussion B, opening the discussion, dealt with the X-ray



spectrometer as an instrument of precision, discussing the nature of the measurements that can be made with it. He compared the possibilities of photographic and ionization spectrometers, dealing with the accuracy obtainable by these instruments. The ionization spectrometer gives observable results more quickly and is far more reliable for the purpose of comparing intensities of lines. The ionization method has been used with excellent results by Duane, Webster, Compton, and others in America; while Dershem, Overn, de Broglie, Hull, and others have used photography. Reference is also made to the work of Wagner, Debye, Leighton, and others. The recent developments in X-ray research were briefly reviewed and the theoretical bearing of the results discussed from the standpoint of at. structure. C. G. DARWIN gave an account of the theory underlying the production of X-ray spectra, the work of Bohr and Sommerfeld receiving special consideration. E. A. OWEN referred to the 4 kinds of frequencies of vibrations associated with X-ray spectra. In the case of the K-series there is or are (1) several emission frequencies, (2) one frequency such that when multiplied by Planck's constant the product is equal to the minimum of energy which the electron in the X-ray tube must have to produce that emission series, (3) one critical absorption frequency, and (4) one critical ionization frequency. A. O. RANKINE referred to the value to teachers of these coördinated accounts of a particular branch of physics. H. G.

**Fine structure of X-ray spectra.** A. SOMMERFELD. *Z. Physik* 5, 1-15 (1921).—S. discusses the weak companions of  $K_\beta$  observed by Hjalmar (C. A. 14, 2750) in the K-series of the light elements. His  $\beta'$  and  $\beta_2$  are probably the same line, so there are really only two companions,  $\beta'$  and  $\beta''$ . The wave-length interval of  $\beta''\beta$  is const. from element to element, as in the "regular" doublets. For  $\beta'\beta$  or  $\beta'\beta''$ , however,  $\frac{1}{\Delta\lambda}$  is approx. linear with the atomic number and S. shows that this is the type of doublet to be expected when the effect of the intermediate  $L$  shells on the transition from  $M$  to  $K$  is taken into account. Considering circular ( $L_1$ ) and elliptical ( $L_2$ ) shells we would have for this "intermediate doublet" differences,  $\Delta\lambda = \frac{q\alpha^2}{4RZ}$  where  $q$  is the number of electrons in  $L$ ,  $\alpha$  the fine structure const.,  $R$  the Rydberg const., and  $Z$  the atomic number. This fits the observed data for  $\beta'\beta''$  well, and thus  $\beta''$  is due to a transition from  $M_1$  to  $K$  with the intermediate shell an  $L_1$ , and  $\beta'$  with this shell an  $L_2$ . This same effect would make the  $K$  absorption limit complex, with a weak absorption max. on the long wave-length side of the principle one, the frequency interval being that of  $\beta'\beta''$ . This is in agreement with what has been observed in the lighter elements by Fricke (C. A. 14, 3363). F. C. HOYT

**Fine structure of X-ray spectra.** II. ADOLF SMEKAL. Vienna. *Z. Physik* 5, 91-106 (1921); cf. C. A. 15, 1855.—S. arranges all the 22 lines in the W L-series in pairs whose frequency differences are equal to those of the absorption limits  $L_1$  and  $L_2$  or  $L_3$  and  $L_4$ . Thus each line can be associated with an absorption limit, in accordance with Sommerfeld's doublet scheme and the critical potential data. A complete "energy level" diagram of the W spectrum is constructed, and it is found there are 5  $M$  levels and 5  $N$  levels. The lines are produced as follows. The notation is that of Coster. K-Series:  $\alpha_1 = L_1$  to  $K$ ,  $\alpha_2 = L_2$  to  $K$ ,  $\alpha_3 = L_3$  to  $K$ ,  $\beta = M_1$  to  $K$ ,  $\beta' = M_2$  to  $K$ ;  $\gamma = N_1$  to  $K$ . L-Series:  $\epsilon = M_3$  to  $L_1$ ,  $\alpha_1 = M_2$  to  $L_1$ ,  $\alpha_2 = M_1$  to  $L_1$ ,  $\beta_1 = N_3$  to  $L_1$ ,  $\beta_2 = N_2$  to  $L_1$ ,  $\beta_3 = N_1$  to  $L_1$ ,  $\gamma = ?$  to  $L_1$ ,  $\eta = M_4$  to  $L_2$ ,  $\beta_4 = M_3$  to  $L_2$ ,  $\gamma_1 = N_4$  to  $L_2$ ,  $\gamma_2 = N_3$  to  $L_2$ ,  $\gamma_3 = ?$  to  $L_2$ ,  $\beta_5 = M_5$  to  $L_3$ ,  $\beta_6 = M_4$  to  $L_3$ ,  $\beta_{10} = M_1$  to  $L_3$ ,  $\gamma_4 = N_4$  to  $L_3$ ,  $\gamma_5 = N_3$  to  $L_3$ . This scheme is tested by several combination schemes and the agreement is satisfactory. A test of the relation  $K_\beta - K_\alpha = L_1 - M_3 = L_1 - L_3 - L_{\beta_4}$  with Hertz data on the L absorption limits of the light elements (C. A. 15, 206) leads to good agreement, and this confirms Kossel's (C. A. 15, 620) association of



$K_{\beta}$  with  $M_2$  as its initial orbit, as opposed to Sommerfeld's placing it with  $M_2$ . III. *M-Series and the selection principle.* *Ibid* 121-9.—The following emission scheme is proposed for the *M-series*:  $\alpha' = N_2$  to  $M_1$ ,  $\beta = N_2$  to  $M_2$ ,  $\gamma = N_2$  to  $M_3$ ,  $\epsilon = N_4$  to  $M_4$ ,  $\alpha = N_1$  to  $M_1$ ,  $\gamma_1 = O$  to  $M_2$ ,  $\delta = O$  to  $M_3$ ,  $\beta_1 = O$  to  $M_1$ . Although uncertain in some details this gives no serious violation of the combination principle and in most cases can be tested through a range of several heavy elements. With the use of three quantum integers to fix each energy level the selection principle holds with this arrangement, the first integer being associated with the azimuthal coordinate. S. also proposes the following empirical rule; In transition between non-hydrogen-type levels of neighboring shells the *third* quantum integer (the one associated with the spacial position) remains unchanged. The best arrangement of the quantum integers between the *M-levels* consistent with the above rules is:  $M_1(3,0,0)$ ,  $M_2(2,1,0)$ ,  $M_3(2,0,1)$ ,  $M_4(1,1,1)$  and  $M_5(1,2,0)$ , also,  $N_1$  is probably  $(4,0,0)$  and  $N_2(3,1,0)$ .

F. C. HOYT

The combination principle in X-ray spectra. D. COSTER. *Lund. Z. Physik* 5, 139-47(1921).—C. believes that the Bohr emission scheme for X-ray spectra should be such that there are no violations of the combination principle, rejecting Kossel's explanation of the "combination defect." With accurate wave-length data it is possible to set up such a scheme. For detg. the initial energy level of a line the critical potential data are used where available, and also the doublet relations. The system thus arrived at is essentially the same as that of Smekal (cf. preceding abstract), giving 3 *M-levels*. C. also gives preliminary data on remeasurements of the *M* absorption limits and has been able to detect all five of these absorption limits in U and Th. The values, which fit quantitatively into the above scheme are;

	$\epsilon_1$	$\epsilon_2$	$\epsilon_3$	$\epsilon_4$	$\epsilon_5$
U	261.03	273.99	317.18	382.1	408.9
Th	241.90	256.55	297.99	354.4	381.6
Bi	191.37	199.45	233 (diffuse)		

The values are of  $\nu/R$ . The  $L\beta$  group in U and Th has also been remeasured, so as to make an accurate test of the above absorption data possible by means of the relations  $M_1 - M_2 = L\alpha_1 - L_1$  and  $M_4 - M_3 = L\beta_1 - L\beta_2$ .

F. C. HOYT

The emission of secondary X-rays in the Coolidge tube. F. CANAC. *J. phys. radium* 1, 123-5(1920); *Science Abstracts* 24A, 274.—A short description of expts. carried out with two Coolidge tubes, details of the differing anticathodes of which are given. Platinocyanide photographs of the secondary emissions are shown. H. G.

Scattering action of special carbon atoms. R. GLOCKER. *Stuttgart. Z. Physik* 5, 54-60(1921).—G. applies his extension of Debye's theory of the scattering of coplanar electron rings (*Ann. Phys.* 64, 511(1921)) to show that the Lande C atom (C. A. 14, 2884) with its spacial arrangement of electron orbits scatters X-rays in essentially the same way as the plane atom. In the outer shells, and independently of the arrangement of the electrons, the scattering coefficient increases much more rapidly with wave length for one-quantum shells than for two. Exptl. data are better in accord with the kind of scattering required by a two-quantum outer shell, but G. regards the question as still uncertain.

F. C. HOYT

The intensity of reflection of X-rays by rock salt. II. W. I. BRAGG, R. W. JAMES AND C. H. BOSANQUET. *Univ. of Manchester. Phil. Mag.* [6] 42, 1-17(1921).—cf. C. A. 15, 1453. The results of the investigation are summarized by the authors as follows: The object of these expts. has been the detn. of the amplitude of the wave diffracted in various directions by the Cl and Na atoms when homogeneous X-rays of unit amplitude fall on these atoms. This amplitude is expressed in terms of that diffracted



ted by a single electron, the results for Cl and Na being shown in fig. 8. The following formulas for the intensity of reflection have been used:  $\frac{E_{\omega}}{I} = \frac{Q}{2\mu}$  for reflexion at a face;  $\frac{E_{\omega}}{I} = Q t \sec \theta e^{-\mu t \sec \theta} \sec \theta$  for reflexion at glancing angle  $\theta$  through a crystal plate of thickness  $t$  cut perpendicular to the reflecting planes.  $Q$  is given by the formula

$$Q = \frac{N^2 \lambda^3}{\sin 2\theta} F^2 \frac{e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \cdot e^{-B \sin^2 \theta}$$

Allowance has been made for the increase in the effective coeff. of absorption  $\mu$ , in the case of strong reflexions, due to the existence of the "extension coeff." The amplitude of the wave diffracted by a pair of Na and Cl atoms is given by the factor  $F \frac{e^2}{m c^2}$ . The two atoms diffract waves which are in phase with each other for all planes except those with wholly odd indices, when the waves are opposed in phase. By measuring the intensity of reflexion for both types of plane, it has been possible to assign values to the amplitude diffracted by the Cl and Na atoms separately over a range of angles from  $10^\circ$  to  $60^\circ$ . The results confirm the accuracy of the measurements and of the theoretical assumptions, since they indicate the correct number of electrons in the atoms of Cl and Na. An estimate of the distribution of the electrons around the nuclei of these atoms may be obtained by analysis of the results, since the forms of the diffraction curves are dependent on the arrangement of the electrons. S. C. LIND

**The constitution of mixed crystals and the space occupied by atoms.** L. VEGARD. Christiania. *Z. Physik* 5, 17-26 (1921); cf. V. and Schjelderup (*C. A.* 11, 2747).—V. uses the crystal powder method of X-ray analysis for investigating the mixed crystal systems: KCl — KBr (cubic), KCl —  $\text{NH}_4\text{Cl}$  (cubic), and  $\text{K}_2\text{SO}_4$  —  $(\text{NH}_4)_2\text{SO}_4$  (rhombohedral). For a mixed crystal the lines are always intermediate in position between those for the pure components, and in no case are there new lines. This means that the substitution of the new component is a wholly random one, as regularities would lead to new lines. For the system KBr — KCl the length of the side of an elementary cube is a strictly additive function of the values for the pure components. S. shows that it follows from the sharpness of the lines that the atoms substituting for each other possess the same diam. in the mixed crystal. The atomic diams. must then be variable within certain limits.  $\text{NH}_4\text{Cl}$  and KCl are of different cubic types, but the mixed crystal of the two is of the KCl type. The  $\text{NH}_4$  has a smaller diameter in the face-centered type of lattice than in the  $\text{NH}_4\text{Cl}$  type. The H atoms are supposed to lie along the cube diagonals. The diams. can then be computed and are found to vary slightly in different lattices.

F. C. HOYT

**Methods for the arrangement of crystal elements.** K. BECKER, R. O. HERZOG, W. JANCKE and M. POLANYI. *Z. Physik* 5, 61-2 (1921).—The authors have investigated (*C. A.* 15, 983) the type of X-ray interference pattern obtained with monochromatic radiation from a mixture of crystals having a definite axial arrangement. Such orientation may be brought about by placing a crystal meal in a magnetic field and also by subjection to pressures of about 5,000 atm. in some cases. Hardening processes for wires also produce this result. F. C. HOYT

**The crystalline structure of antimony and bismuth.** A. OGG. Univ. of Cape Town. *Phil. Mag.* [6] 42, 163-6 (1921).—The Bragg X-ray spectrographic method was employed in studying the crystal structure of Sb and Bi. For Sb the expts. confirm the expts. of James and Tunstall (*C. A.* 14, 3585) that the unit rhomb contains 8 atoms, that the length of the edge of the unit rhomb is  $6.20 \text{ \AA}$ . U., and that the structure consists of two interpenetrating face-centered lattices. The spacings of the planes, which



differ somewhat from those of J. and F., are shown by a diagram. The shortest distance between the centers of two atoms is 2.92 Å. U. For Bi the unit rhomb also contains 8 atoms, the length of the rhomb is 6.52 Å. U. The spacings of one of the face-centered lattices have been calcd. taking the structure of cryst. Bi as similar to that of Sb. The relative positions of the two sets of planes were not accurately fixed on account of the faintness of the spectra.

S. C. LIND

The crystalline structure of bismuth. R. W. JAMES. Univ. of Manchester. *Phil. Mag.* [6] 42, 193-6(1921).—The cryst. structure of Bi has been detd. by the Bragg X-ray spectrometer method. Bi like Sb crystallizes in the di-hexagonal alternating class of the hexagonal-system. The symmetry is that of the rhombohedron. The length of edge of the unit structure is  $3.23 \times 10^{-8}$  cm. The closest approach of the atom which may be regarded as the diameter is 3.11 Å. U. For Sb it is 2.87 Å. U.

S. C. LIND

Formation of crystals by directed vapor molecules. M. VOLMER. Hamburg. *Z. Physik* 5, 31-4(1921).—A stream of Cd vapor sublimed in a high vacuum from a heated piece of the metal is made to strike at an angle on a piece of glass. The resulting deposit, when microscopically examined, is found to consist of crystal particles of Cd. with their 0001 faces oriented in one plane so as to form a reflecting surface. V. concludes that the particles in the vapor stream had this orientation. The phenomenon is unaffected by a counter stream of H.

F. C. HOYT

Formation of crystals by directed vapor molecules. R. GROSSAND AND M. VOLMER. *Z. Physik* 5, 188-91(1921); cf. preceding abstract.—Goniometer measurements to fix the reflecting planes confirm the previous statement that the condensation of the vapor stream gives a crystal deposit whose individuals have a regular orientation within narrow limits.

F. C. HOYT

Physical theory of stellar spectra. M. N. SAHA. *Proc. Roy. Soc. (London)* 99A, 135-52(1921).—By means of the ionization-potential for the series lines of various elements, S. computes the temp. which would give rise to these lines at atmospheric pressure and at one tenth atm. Then by noting the presence or absence of these lines in stellar spectra the temps. of stars of the various stellar classes are estimated. The results are in fair agreement with those derived by radiation methods, the most important difference being the higher temp. found for the red stars by the present method.

K. BURNS

Criticism of Bohr's theory of the emission of light. J. STARK. *Jahrb. Radioakt. Elektronik* 17, 161-73(1920); cf. Sommerfeld, *Atombau und Spektrallinien* (C. A. 14, 690).—A criticism of Bohr's theory of the emission of light in which it is shown that this hypothesis has been able to give a quant. deduction of the Balmer series formula and thereby the Rydberg const., a quant. representation of the effect of an elec. field on the H series lines both with regard to the number and sepn. of the components, and also a deduction of the Zeeman triplets. These 3 services are obtained by means of 3 unsatisfactory assumptions, so that the solution of 3 difficulties has been obtained by the introduction of 3 new difficulties. The Bohr hypothesis proves the existence, in opposition to a number of observations, of the Doppler effect with canal rays, continuous spectra of atoms, the intimate structure of H and He lines, the Zeeman effect of neighboring line components in strong fields, while it does not indicate the dissymmetry of the intensity in the effect of the elec. field on the H series lines.

J. C. S.

Doublets in spectral series. D. ROGESTVENSKY. *Nature* 107, 203-4(1921).—Wood and Mohler (*Phil. Mag.* 37, 456(1919)) found a limiting value of 2, for the ratio  $D_2/D_1$ , when Na vapor is excited by D<sub>1</sub> light. R. calls attention to work published in Russia in 1915 and 1917, in which this ratio was investigated from the dispersion of the vapor of the various alkali metals, with large density variations. A const. ratio of 2



was obtained for the first doublet of all the alkalis, but various simple numbers (2 to 7) in the case of the second and third doublets. The ratio seems to be a statistical value which first increases rapidly with temp. and then approaches a limiting value, essentially const.

R. T. BIRGE

**Power of emission of the metals and methods for its determination.** F. HENNING. *Jahrb. Radioakt. Elektronik* 17, 30-62(1920).—A theoretical discussion on the emissivity of metals in which it is shown from the investigations of Hagen and Rubens (*C. A.* 3, 508; 4, 1571, 2599), that the formula  $A = 1 - R = 0.365 (\gamma/\lambda)^{1/2} - 0.0667 \gamma/\lambda + 0.0091 (\gamma/\lambda)^{3/2} - \dots$  and  $A = 0.365 \sqrt{\gamma/\lambda}$ , in which  $A$  is the power of absorption and  $R$  the reflection, represent the absorptive power of the metals for long wave lengths ( $26\mu$ ). At the wave length  $\lambda = 8.85\mu$  marked deviations from the theory are already observed, which, however, only show themselves in the abs. quantity and do not appear in the temp. coeff. of the absorptive power. The temp. coeff. is still in fair agreement with theory for wave lengths  $4-5\mu$ , but on passing to still shorter wave lengths it suddenly deviates from the theoretical value, and at  $2\mu$  the absorptive power of the metals is independent of the temp., while at longer wave lengths it has a positive temp. coeff. The absorptive power of Ta and the Pt metals in the visible spectrum is const. In the case of W, exptl. results of various observers are at variance; some regard it as const. while others assign a negative or a positive temp. coeff. to it. The radiation properties of W are very much influenced by impurities, and this probably accounts for the above-mentioned diversity in the results. Many observers have found that molten Au, Ag, Cu, Ni, Pd, and Pt have a stronger power of emission in red light and a weaker power of emission in blue light than the solid metals, while in the case of molten W Langmuir (*C. A.* 9, 2619) has found that it radiates more weakly in red light than the solid metal, while Bidwell (*C. A.* 8, 2834) found a difference when only O was present. In calcg. the intensity of radiation in the visible region the following values of the power of emission are recommended where the  $\lambda$  values are given in 0.001 mm.  $\lambda$ , 0.45, 0.50, 0.55, 0.60, 0.65, 0.70; Ag, 0.10, 0.09, 0.07, 0.06, 0.05; Au, 0.67, 0.53, 0.26, 0.16, 0.11, 0.08; Pd, 0.33; Pt, 0.45, 0.42, 0.39, 0.36, 0.33, 0.31; Rh, 0.24, 0.23, 0.22, 0.21, 0.20; Ir, 0.28, 0.27, 0.25, 0.24; Ta, 0.62, 0.60, 0.58, 0.56; W, 0.52, 0.51, 0.50, 0.49, 0.47, 0.46. J. C. S.

**The spectrum of helium in the extreme ultra-violet.** HUGO FRICKE AND THEODORE LYMAN. *Harvard Univ. Phil. Mag.* [6] 41, 814-17(1921).—Previous study of the spectrum of He by L. in the Schumann region (*C. A.* 6, 1091; 10, 2067) furnished results which were difficult to interpret and later investigations have indicated that several of the lines observed were due to impurities. A new detn. has been made with an improved vacuum spectroscopy with a grating of only 20 cm. radius with a dispersion of 84.6 Å. per mm. which extended to 1200 Å. The strongest line on all the plates was 585 Å. The other lines usually present were lacking and are due to impurities. The line 585 corresponds to the voltage 21.2. This line alone and not the one for 20.4 agrees with other work.

S. C. LIND

**Interpolation table for the calculation of spectral series.** ANGEL DEL CAMPO AND MIGUEL CATALÁN. *Anales soc. española fis. quim.* 18, 118-28(1920).—Rydberg's tables for the calcn. of spectral series are recalc., with the more recent value for the const.  $N$ , found by Curtis (*C. A.* 9, 18).

J. C. S.

**Wave lengths of lines in the iron arc from grating and interferometer measurements,  $\lambda 3370-6750$ .** CHARLES E. ST. JOHN AND HAROLD D. BARCOCK. *Astrophys. J.* 53, 260-99(1921).—The source used was the 12-mm. 5-amp. Pfund arc, which yields sharper and more dependable lines than the arc which has been generally used hitherto. This increased sharpness applies particularly to those lines which are most affected by pressure shifts and whose wave lengths vary with the type of arc and the part of the arc used. The greater portion of the 1026 lines tabulated were measured both by means



of gratings and by interferometers. Four sets of interferometer plates were employed, and five excellent gratings, two by Michelson and three by Anderson. By internal agreement and by comparison with the tables of the Bureau of Standards the accuracy is shown to be of the order of  $0.001 \text{ \AA}$ . For the classes of lines whose wave lengths are most sensitive to the conditions of the source the differences arising from the use of different types of arcs are clearly shown. The article contains useful hints concerning the reduction of measurements and discusses the relative advantages of the grating and interferometer.

K. BURNS

**Quantitative knowledge of the cesium spectrum.** HANS BARTELS. *Ann. Physik* 65, 143-66(1921).—Cs was vaporized in an elec. furnace at temps. from  $190^\circ$  to  $232^\circ$ . The absorption spectrum was photographed by means of a concave grating on a scale of  $1.8 \text{ \AA}$  per mm. A spiral-filament tungsten lamp served as source of the continuous spectrum. The percentage absorption and the width of the lines were measured for the lines  $\lambda 3617$  and  $\lambda 3612 \text{ \AA}$ , the components of one member of the doublet series. The vapor pressure was computed from the known tension at  $233^\circ$ , assuming that absorption is proportional to pressure. The values are 0.046, 0.068, 0.084, and  $0.211 \text{ mm.}$  of Hg for the temp.  $191^\circ$ ,  $199^\circ$ ,  $205^\circ$ , and  $232^\circ$ . These data show that the absorption method is a very sensitive means of detecting small quantities of Cs vapor. The relative intensities of the two components are in agreement with the law: For the doublets of the alkali series the coeff. of the max. absorption of the violet component is  $m$  times that of the red component,  $m$  being the term number in the series. A comparison with earlier work on other members of the series indicates that the lines broaden rapidly with increasing term number.

K. BURNS

**The iodine molecule and the emission of its band spectrum.** W. STREUBING. *Ann. Physik* 64, 673-92(1921).—S. has already shown (*C. A.* 14, 1931) that a magnetic field causes a weakening of the fluorescent band spectrum of I vapor. In the present work an attempt is made to obtain this same band spectrum in other ways, and to examine the magnetic effect. The spectrum could not be obtained in flames, nor in a satisfactory condition, in vacuum tubes with metallic electrodes. But in the positive column of a vacuum tube, with graphite electrodes and high-tension direct current, the spectrum appeared very strongly. It showed optical magnetic effects similar to those of the fluorescent spectrum, and in addition a mechanical magnetic effect, diamagnetic in character. Detailed investigation, as explained fully in the article, led to the following conclusions:—(1) the band spectrum is associated with the iodine mol.; (2) it is produced through the uniting (in a definite manner) of a negative electron with the molecule. It is immaterial, optically, whether the electron comes from the molecular union itself (through fluorescence), or as a free electron from the outside; (3) an external magnetic field accelerates the re-combination; (4) during the process of re-combination, in the case where the electron comes from the outside, and during the simultaneous emission of the band spectrum, the system experiences a diamagnetic mechanical reaction. During this time the system must, however, be considered electrically neutral; (5) this semi-ionized condition lasts for a finite time, since the system, as a result of the diamagnetic effect, produces a definite mechanical pressure on surrounding bodies; (6) from the length of the radiating column of vapor, in a specially constructed tube, the duration of this semi-ionized condition is estimated at about  $5 \times 10^{-10} \text{ sec.}$ , i. e., longer than the probable period of fluorescence.

R. T. BURG

**Spectrum of bromine vapor; Zeeman effect.** G. RIBAUD. *J. phys.* 7, 205-8 (1917); *Science Abstracts* 24A, 260. Emission spectrum. With a Geissler tube discharge given by an accumulator battery, the tube having a large enough capillary, a spectrum of Br vapor consisting of a large number of lines is obtained. The relative intensity of these lines depends on the conditions of the discharge. If the intensity



of the discharge is increased, certain lines are reinforced, while others disappear. The addition of a capacity across the tube also causes some lines to disappear. *Zeeman effect.* If a Geissler tube is placed perpendicularly to the field of the electromagnet and strong fields are used, the apparent resistance of the tube becomes extremely high and the discharge requires, therefore, a very high potential. Moreover, the lines obtained are much broadened and difficult to measure. A tube was consequently introduced along the axis of the pole-pieces. The holes through the ends of the pole-pieces were about 7 mm. in diam. for about 2 cm. and then about 2 cm. diam., so that the capillary portion was very short, and the tube resistance as low as possible. Twenty-six lines were studied in the region  $\lambda 4014$  to  $\lambda 5332$ , a Rowland concave grating being employed. The field, as measured by the Zeeman effect on the Zn line  $\lambda 4680$ , was found to be 21,800 gauss. The values of  $\Delta\lambda/H\lambda^2$  for the majority of the lines are grouped about the values  $1.05 \times 10^{-4}$  and  $1.23 \times 10^{-4}$ . Normal sepn. was not observed for any of the lines, but three of the lines  $\lambda 4766$ ,  $\lambda 4785$ , and  $\lambda 4816$ , have a sepn. very nearly double the normal. (Cf. C. A. 7, 1136; 15, 984.) H. G.

Some phenomena of laminar diffraction observed with mica. P. N. GHOSH. *Indian Assoc. for Cultivation of Science, Proc.* 6, 1 and 2, 51-65 (1920); *Science Abstracts* 24A, 180.—In a previous paper (*Proc. Roy. Soc. (London)* 96A, 257-66 (1919)) G. described and explained the colors shown by the striæ or laminar boundaries in mica when it is exanid. by the Foucault test. The present paper describes some observations on the microstructure of these laminar boundaries and of the various diffraction effects produced by them. The following are the principal results obtained. (1) The striæ appear resolved in the microscope into minute echelons or staircase structures, the number of steps varying from 1 to 10 or 15 for different striæ. The optical retardation due to any particular edge in the echelon is generally quite a small fraction of a wave length. The edges are nevertheless clearly visible in the microscope as very sharp dark lines. *Asymmetry in distribution of color of the fringes and method of exhibiting same.* (2) In consequence of the structure of the striæ, the laminar diffraction pattern observed even at a considerable distance from the mica shows distinct evidence of a symmetry in the distribution of intensity and color of the fringes. A very delicate method of exhibiting this asymmetry is furnished by spectroscopic analysis of the laminar diffraction pattern, the dark bands due to interference running obliquely through the spectrum, and being much more clearly marked on one side of the pattern than on the other. (3) In the immediate neighborhood of the striæ the diffraction phenomena as observed through a microscope are more complicated, the asymmetry being very marked, and a very large number of fringes may be observed. (4) The striæ scatter light through large angles, the light thus diffracted showing a marked asymmetry in its intensity on the two sides of the direction of the incident light, and also exhibiting both color and polarization. Photographs of the various effects are reproduced. H. G.

The use of a lime cathode of carbon in spectroscopy. Y. SUGIURA AND T. MATOBA. *Astrophys. J.* 53, 323-5 (1921).—A thin strip of hard carbon is soaked in a soln. of Ca and Ba nitrate and dried. This is heated in vacuum and used as cathode. A p. d. of a few hundred volts causes an electronic current sufficient to melt small quantities of refractory materials on a neighboring anode or to give an intense line spectrum of the anode metal. This source facilitates the study of the structure of the lines of Cd, Bi, etc., by means of high resolution. A plate illustrates the results that may be obtained in the case of the Bi lines by the use of a Lummer-Gehrcke plate. K. BURNS

Spectrochemistry of cyclobutane derivatives. G. J. ÖSTLING. *Finska Kemist-seminfundels Medd.* 1916.—Three cyclobutane derivs. were exanid. spectrographically. *Methyl pinate*,  $C_{11}H_{18}O_4$ ,  $b_{11}$  125.4-6.2°,  $d_4^{14.3}$  1.0360, does not decolorize  $KMnO_4$  in alk. soln. *Ethyl pinate*,  $C_{13}H_{20}O_4$ ,  $b_1$  136-136.5°  $d_4^{14.4}$  1.0174; *methyl ropate*,  $C_{11}H_{18}O_4$ ,



$n_D^{20} 1.36^\circ, /d_4^{20} 1.0875$ , decolorizes  $KMnO_4$  slowly. The refractive indices for the three compds. were found, using different wave lengths. J. C. S.

The physical significance of the least common multiple. NORMAN CAMPBELL AND E. C. C. BALY. *Phil. Mag.* [6] 41, 707-16(1921).—A note states that the paper is the result of a long private discussion between its authors in which some of their differences have been resolved, but since a residuum of disagreement remains, their views can be expressed in the form of a criticism (by Campbell) and a reply by Baly. Campbell states that Baly's (*C. A.* 14, 3586) interpretation of his work on absorption spectra is the first attempt to attribute a physical significance to the least common multiple and, therefore, requires some examn. C. points out that only commensurable frequencies can have a L. C. M. Waiving the point as to whether absorption spectra are commensurable in the sense of the Balmer series lines, Campbell points out that in order to have a true L. C. M. there is no allowable error in the two values going to make up the multiple; otherwise, an infinite uncertainty is introduced as to the L. C. M. Concrete examples are given by C. supporting his arguments, and it is pointed out that by varying the scale of notation a very different L. C. M. is obtained for the same data. C. concludes that there are only two alternatives (1) that B.'s agreements are coincident, or (2) that all exptl. physics is founded on a delusion and that scales of notation have physical significance. In his reply, B. admits the general validity of C.'s arguments, but claims that the agreements are too close and too numerous to admit of their being merely coincidental. B. presents the evidence in favor of the existence of a fundamental energy unit which he believes is possibly the elementary quantity of energy characteristic of the H atom. Examples are cited from recent works on the radiation theory of chem. action and the Einstein photochem. equivalence law to support B.'s hypothesis. S. C. LIND

Infra-red absorption spectra of solids in thin layers. O. REINKOBER. Danzig-Langfuhr. *Z. Physik* 5, 192-97(1921).—R. uses thin layers condensed on transparent plates from the sublimed or vaporized substance. The absorption spectra of the  $NH_3$  halides are investigated to  $8\mu$  and a few new weak characteristic frequencies noted.

F. C. HOYT

Absorption of light; width of absorption bands in different regions of the spectrum. G. RIBAUD. *Compt. rend.* 171, 1134-6(1920); *Science Abstracts* 24A, 178-9; cf. *C. A.* 15, 19.—This paper deals with the broad continuous regions of absorption shown by gases, liquids, and solids. After briefly indicating the exptl. laws hitherto known, expts. are referred to which lead to the conclusion that for the same substance in different physical states, or for the same chem. group in different compds., the max. of the continuous region of absorption is more displaced towards the long wave lengths the greater the value of the max. absorption. Other expts. have shown that at a given temp., the damping in an absorption band only depends on the position of this band in the spectrum. In other words, if two bodies have an absorption band in the same region of the spectrum, the dampings, or what comes to the same thing, the widths of their bands, are the same. Numerous verifications of this principle have been made. The width  $\delta$  of an absorption band, which is solely a function of its position in the spectrum, increases continuously on going from the ultra-violet towards the infra-red, very nearly proportionally to the wave-length max. For  $\lambda_m = 2700 \text{ \AA}$ ,  $\delta = 420 \text{ \AA}$ , and  $\lambda_m/\delta = 6.4$ . For  $\lambda_m = 5000 \text{ \AA}$ ,  $\delta = 770 \text{ \AA}$ , and  $\lambda_m/\delta = 6.5$ . For  $\lambda_m = 33,000 \text{ \AA}$ ,  $\delta = 72000 \text{ \AA}$ , and  $\lambda_m/\delta = 4.9$ . It is interesting to note that for all the ultra-violet and visible bands studied the observed widths of the absorption bands furnish a damping coeff.  $r$  (defined by the relation  $(m\delta^2x/dt^2) + (mr\delta x/dt) + m\omega_m^2x = h\nu$ ) very approx. equal to the frequency. H. G.

The absorption of ultra-violet and infra-red radiations by glasses. A. W. SMITH AND C. SHERRARD. *J. Optical Soc. Am.* 2-3, 26(1919); *J. Soc. Glass Tech.* 3, 253.—



Twenty-nine glasses, designated variously as Euphos, Amethyst No. 1, Dark Amber, and so on, no comps. being given, were examd. A photograph, taken with a Péry quartz spectrograph, registered the transmissions in the ultra-violet. As the specimens were of different thicknesses, and the source of light (a condensed spark between electrodes of Fe and an alloy of Cd, Al, Mg, and Zn) was unsteady, the results were not comparable. The "amethyst" glasses transmitted farthest into the ultra-violet, their limit being about  $0.319\ \mu$ . Noviol *b* was the least transparent, absorbing all rays beyond  $0.5\ \mu$ . A Hilger infra-red spectrometer was used for the transmissions in the infra-red region. Transmission curves ranging from  $\lambda=0.75\ \mu$  to  $4.75\ \mu$  were given for all the glasses except one, namely, "Pfund" glass, which absorbed the infra-red to such an extent that no transmission was measurable. A Nernst glower was used as the source of the radiations. All the curves were similar in that a large increase in the absorption took place at  $\lambda=3\ \mu$  until it was nearly total at  $\lambda=4\ \mu$ . Near the visible region many of the glasses showed selective absorption. H. G.

The absorption spectrum of hydrogen chloride. WALTER F. COLBY and CHARLES F. MEYER. *Astrophys. J.* 53, 300-9(1921).—The HCl absorption band extending from 3.16 to  $3.70\ \mu$  was observed by app. similar to that described by Imes, (C. A. 14, 3366). The compensation chamber was found to be superfluous. The absorption chambers, 16 to 60 cm. in length, could be heated to incipient redness. The expts. confirmed results of Paton showing that heating increases the number of observable lines but does not change the wave length. The wave numbers for 28 lines were tabulated and an equation was derived to represent them. The law of spacing is not parabolic, as has been supposed, but a cubic term is found to be necessary. K. BURNS

Influence of increased temperature on the fluorescence and absorption of iodine vapor of constant density. P. PRINGSHEIM. Berlin. *Z. Physik* 5, 130-8(1921).—P. measures with a high dispersion both the absorption and the fluorescent emission spectrum of I vapor sealed into a glass tube and heated, the density remaining const. There proves to be a change in the emission spectrum itself with temp., and also in the absorption. The increased secondary absorption in the short wave-length end of the band spectrum accounts for the change from green to blue observed when the density of the vapor is increased. The similar phenomenon observed with pure temp. increase is attributable to diminished primary absorption and the consequent diminution of fluorescence in that spectral region. There are not only an intensity shift in the total absorption spectrum, but considerable changes in the energy distribution within individual bands. F. C. HOYR

The action of light on sparingly soluble oxides in solutions of silver salts. G. TAMMANN. *Z. anorg. allgem. Chem.* 114, 151-2(1920).—When ignited ZnO is left in a soln. of AgNO<sub>3</sub> or Ag<sub>2</sub>SO<sub>4</sub> in subdued light, it remains white for a whole day, but in bright light it quickly becomes gray, and, after a quarter of an hr., black. PbO (litharge) blackens in the same manner, even in subdued light, but less rapidly than in sunlight, and Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, and yellow HgO change in color more slowly. The blackening is due to the deposition of Ag oxide. An ionic exchange appears to take place at the surface of the oxide, controlled, probably, by the elec. potentials of the reacting substances. The velocity of the reaction depends on the tendency of the Ag oxide to crystallize in the lattice form appropriate to the medium in which the deposition takes place. J. C. S.

Ultra-violet and visible transmission of various colored glasses (GIBSON, ET AL.) 19.  
Point discharge in nitrogen (PIRANI, LAX) 2. Magnetization of gases and the magneton (BAUER, PICCARNI) 2. Synthetic helium and neon (LOSDORF) 2. Photo-bromination of toluene and xylene (SWENSSON) 10.



## 4—ELECTROCHEMISTRY

COLIN G. FINK

Harris Joseph Ryan. ANON. *Elec. World* **78**, 202, 240(1921); 1 illus.—Biographical sketch. C. G. F.

Francis Bacon Crocker. ANON. *Elec. World* **78**, 134-5(1921); 1 illus.—Died July 9th, 1921. Eulogies by S. S. Wheeler, T. A. Edison, *et al.*, are appended: Crocker did "brilliant work in his design of elec. motors, the arc furnace and in the chemistry of the primary battery." (See also *Elec. Rev.* **79**, 144(1921)). C. G. F.

Electrometallurgy in America. H. P. MARTIN. *Forno elettrico* **3**, 3-5(1921).—A review. C. G. F.

Electrochemistry and electrometallurgy in France in 1920. M. DE MONTLAUR. *J. Jour électrique* **30**, 64-5(1921).—A review. C. G. F.

Electrometallurgy of the light metals during the past ten years. F. PEYERS. *Glückauf* **56**, 514-7(1920).—A review. C. G. F.

The metallurgy of the electric pig iron furnace. R. DURRER. *Stahl u. Eisen* **41**, 753(1921).—The greatest difference between electrical heating and blast heating is in the amount of gas produced. In the ordinary blast furnace 4500 cu. m. of gas are formed for every ton of pig iron smelted, while with the elec. pig Fe furnace only 600 cu. m. are formed. The temp. at the hearth of the two furnaces is practically the same but the greater amount of gas in the ordinary blast furnace heats up the charge in the boshes and stack much more. The temp. gradient from hearth to throat is accordingly much greater in the elec. furnace. This causes the indirect reduction of the Fe oxide to be a much smaller proportion of the total reduction than in the ordinary blast furnace. The throat gases of the elec. furnace are accordingly much richer in CO which is an advantage if they can be used economically. The comparative compositions of the throat gases are: elec. furnace, 61% CO, 22% CO<sub>2</sub>, 12% H<sub>2</sub>, 2% CH<sub>4</sub>; blast furnace, 28% CO, 10% CO<sub>2</sub>, 3% H<sub>2</sub>, 1% CH<sub>4</sub>, 58% N<sub>2</sub>. The elec. furnace may be considered as an economic possibility only when elec. energy is proportionately cheaper than coke. R. S. D.

Problem of pig iron production in the electric furnace. MARCELLO GUÉDRAS. *Giorn. chim. ind. applicati* **3**, 104-5(1921); cf. C. A. **15**, 2581.—A critical consideration of the factors involved in the process, *i. e.*, consumption of energy, low consumption of coke, production of gas of high calorific power. Cf. *Löffler, Teknisk Tidskrift* **51**, 50(1921). ROBERT S. POSMONTIER

Acid or basic electric furnaces. F. W. BROOKE. *Mining and Met. No.* **174**, p. 49; *Canadian Foundryman* **12**, 30 1(1921).—See C. A. **15**, 2253. C. G. F.

The electric furnace as a central station load. H. A. WINNE. *Gen. Elec. Rev.* **24**, 510-514(1921).—On Jan. 1, 1921, 356 elec. steel furnaces were installed or contracted for in the U. S. and it is estimated that in 1925, assuming normal growth, the total transformer capacity of elec. steel furnaces installed will reach 450,000 kv. a. with a general power consumption of 500,000,000 kw. hr. with an additional 350,000,000 kw. hr. for non-ferrous metal melting. The power factor of the furnace load will, as a rule, average at least 85%, considerably higher than the overall motor load. Elec. brass melting furnaces are even better loads than steel furnaces, being in smaller units, and supplying a better load factor. The increased use of improved induction furnaces for both high grade steel and non-ferrous work is predicted. W. E. RUDER

Electric furnaces for making steel. II. ALFRED STANSFIELD. *Blast Furnace Steel Plant* **9**, 263-6(1921); cf. C. A. **15**, 1462.—The *Rennerfelt* elec. furnace is a second type of the independent arc furnaces. It has 3 electrodes, 2 horizontal and 1 vertical, the vertical electrode serving as the common return for the 2 phases supplied to the other 2 electrodes. The magnetic force exerted by the current in the vertical



electrode forces the arc directly downward and thus heats the charge more directly than the Stassano furnace. Early types of the Rennerfelt furnace were cylindrical but later forms are circular in plan with an arched roof. The latter form permits of more easy repairs. In earlier furnaces the lateral electrodes were horizontal or slightly inclined downward but incapable of vertical adjustment. The present arrangement allows vertical adjustment. The electrodes can be raised to accommodate a full charge and, as the charge melts lowered to keep the arc close to the metal. After the charge is melted the electrodes can be lowered until the arc passes from each electrode to the slag and metal so that the advantage of direct arc heating can be secured during refining. Up to the present time Rennerfelt furnaces have been made in small and moderate sizes, the largest having a capacity of 3 to 4 tons and 800 to 900 kv. a. The av. values for operating data from several heats in a steel foundry using an acid-lined R. furnace, operated during the daytime only, were, wt. of charge 1831 lbs., time 3.5 hrs., power consumption 637 kw. hrs. per ton, electrode consumption 8 to 11 lbs. per ton. Refining steel (taking off 1 slag) in a 300 kw. basic-lined furnace operated continuously required 670 kw. hrs. per ton. There are now 150 Rennerfelt furnaces in operation and under construction throughout the world. Power consumption in kw. hrs. per metric ton for melting of product is given for red brass as 168; Cu 197; white Fe 290; gray Fe 325; 80% Fe-Mn 411; steel scrap not ready to pour 455; steel scrap, melting and killing on acid bottom, 600; steel scrap melting and refining on basic bottom, 700; 80% Fe-Mn melting holding, tapping and charging 741; making 67% Fe-W 5730. A short bibliography on the Rennerfelt furnace is appended.

LOUIS JORDAN

**The electric furnace in the iron foundry.** (Discussion). RICHARD MOLDENKE. *Trans. Am. Inst. Mining Met. Eng.* No. 1073, 73-7(1921); cf. *C. A.* 15, 1104.—Geo. K. ELLIOT believes there are 3 classes of Fe castings for which the elec. furnace is an economic feasibility: (1) Castings in which unusual physical properties are desired above all else. (2) Castings that, on account of thinness of section, are ordinarily run only with excessive losses through "cold shuts" and other manifestations of Fe lacking in fluidity. (3) Castings that may require considerable expensive machining before possible defects are revealed. The elec. furnace brings about a great reduction in shop defectives in such castings. W. N. CRAFTS finds that refining in a basic elec. furnace to remove S will result in a metal hotter than it should be for good pouring. A. L. STILLMAN considers the present limit of the utilization of cast Fe boring briquets in the cupola about 20%. In duplexing methods we can hope for at least 40%. R. MOLDENKE repel that a superheated charge can readily be allowed to stand until cool enough to pour or the superheat can be cut down by the addition of cold sprues. Alloying metals as Ni, Cr, etc., should enter the cast Fe by way of the blast furnace rather than as ferro alloys. H. A. SCHWARTZ said that the field of improving cast Fe by elec. furnace melting is hardly limited to the removal of S and O but rather extends until the elec. furnace becomes the means of quant. control of the various elements alloyed with Fe toward the attainment of desired physical properties.

LOUIS JORDAN

**Electric forging furnaces.** ANON. *Elektrotechn. Anzeiger* 38, 361(1921).—A review. C. G. F.

**Manufacture of ferro-manganese in the electric furnace.** (Discussion). ROBERT M. KEENEY AND JAY LONERGAN. *Trans. Am. Inst. Mining Met. Eng.* No. 1073, 68-73(1921); cf. *C. A.* 15, 1656.—J. W. RICHARDS suggests that increasing the  $Al_2O_3$  in the slag may decrease the amt. of Mn going into the slag and at the same time avoid the difficulty of the formation of  $CaC_2$  which results when  $CaO$  is added in order to decrease Mn in the slag. The use of the *Söderberg electrode* (*C. A.* 14, 247, 3018) may reduce electrode costs 50%. The construction of this electrode is described in detail.



E. S. BARDWELL disagrees with equations indicating the reduction of  $\text{MnCO}_3$  by C. Furnace conditions are such that  $\text{MnCO}_3$  is calcined to  $\text{MnO}$  and the latter is then reduced by C. There is no reason for introducing Si into the reaction. B. suggests proportioning the electrodes on the basis of energy density rather than current density, e. g., 1 sq. in. of cross-sectional area for every 0.75 kw. input. K. and L. in comparing the elec. furnace to the blast furnace have possibly understated the case. Small furnaces of 1100 kw. input have consistently made 90% recoveries even on low grade ores.

LOUIS JORDAN

Notes on the metallurgy of calcium. P. H. BRACE. *Chem. Met. Eng.* 25, 105-9 (1921).—See C. A. 15, 1237.

E. H.

The electrolysis of alkali chlorides. R. MORITZ. *Chimie industrie* 5, 636-41 (1921).—Notes on the operation of Type PbF B Moritz cells, under conditions where elec. energy was relatively cheap, coal very expensive, salt fairly cheap, while the NaOH could be used dil. and containing large amts. of NaCl. If the concn. of the liquor is allowed to fall in the cell, the voltage rises, the current and energy efficiency drop, the quantity of  $\text{H}_2\text{O}$  to evap. from the NaOH increases, and the loss of Cl through the diaphragm increases. Increasing the c. d. increases the power consumption and also the wear on the graphite anodes. The latter may be reduced by placing the electrodes close to each other, impregnating the anodes to prevent penetration by the liquor, and completely removing sulfates from the brine and preventing the formation of chlorates. The diaphragm must be so constructed that the coeff. of filtration at the top is about the same as at the bottom, and that it remains approx. const. in spite of the gradual clogging up of the pores. By protecting the diaphragm with a coarser filtering surface and by maintaining a warm moist atm. on the side of the cathode which is not working, the life of the diaphragm is considerably prolonged.

A. P.-C.

A twelve circuit battery charging board. ANON. *Elec. Rev.* 79, 106(1921).—Detailed illus. description.

C. G. F.

Some improvements in the Poulsen arc. P. O. PEDERSEN. *Electrician* 86, 634-6, 714-6(1921).—P. gives a short résumé of his investigations on the Poulsen arc. As a result of these investigations a water-cooled Cu shoe is used on the C cathode. This shoe makes possible one-peak working of the arc by extinguishing the arc when it has traveled a definite distance along the electrode.

D. MACRAE

Mercury arc rectifier vs. rotary converter. ANON. *London Elec. Times* June 9, 1921; *Elec. World* 78, 231(1921).—The operation of the first steel cylinder Hg arc rectifier in England is described. It is shown that the rectifier is more efficient than the converter.

C. G. F.

Extrapolation and calculation of the concentration and yield of ozonizers. H. BECKER. *Wiss. Veröffentl. Siemens-Konzern* 1, 76-106(1920).—The efficiency of an ozonizer is detd. by the concn. and yield of  $\text{O}_3$  obtained when the app. is worked under definite conditions of frequency, tension, temp., humidity of the air or  $\text{O}$  employed, and velocity of gas in the ozonizer. In order to reduce the time necessary for the detn. of the characteristic curves of an ozonizer, showing the relations of the concn. and yield of  $\text{O}_3$  resp. to the gas velocity, a method whereby the efficiency of the ozonizer at high velocities may be extrapolated from results obtained at low velocities is described. For certain velocities, the expenditure of energy in the ozonizer appears to be const. A comparison of two ozonizers can be made on their respective expenditure of energy per unit vol. of reaction space, which may be termed the wattage density. It is recommended that where a. c. of 500 frequency is available, or where the cost of elec. power is low, the ozonizer should be worked at the highest wattage density possible. Where a. c. of frequency 50 only is available, a small wattage density should be chosen for working the ozonizer. Expts. showed that from 30 to 35% of the energy supplied to an ozonizer



was absorbed by the glass walls of the app. This loss diminished with continued working of the ozonizer. When the wattage density employed exceeded a certain value, the concn. of  $O_3$  diminished. J. C. S. I.

The theory of antenna radiation. A. P. KESS. *Electrician* 87, 10(1921).—A brief note discussing the "galvanic" and "voltaic" effects. C. G. F.

Transformer tanks of copper-alloy steel. R. V. BINGAY. *Elec. Rev.* 79, 102(1921).—Steel containing from 0.15 to 0.25% Cu on account of its resistance to corrosion adds to the life of transformer tanks and helps to insure continued service under adverse atm. conditions. Cf. D. M. Buck, *C. A.* 15, 2626. C. G. F.

Chart showing apparent resistance of large copper cables. T. H. ARNOLD. *Elec. World* 78, 28(1921). C. G. F.

Hydroelectric development at Niagara Falls. JOHN L. HARPER AND J. A. JOHNSON. *J. Am. Inst. Elec. Eng.* 40, 561-76(1921). C. G. F.

Electrolytic preparation of cuprous oxide. J. OKAYA, G. KIKUCHI and K. ISHII. Japan 36,551, June 11, 1920. In the electrolytic prepn. of  $Cu_2O$ , with Cu as negative pole, a satd. soln. of NaCl as electrolyte and current of 2 v. and 50 amp. per sq. ft. at 60°, the negative pole is packed with parchment paper, asbestos or pieces of porous earthenware, by which formation of reduced Cu is prevented.

Apparatus for regulating the hydrochloric acid content of an electrolytic bath for alkali chlorate. GENZABURŌ ARAI and TAKASAGO SUIRYOKUDENKI Co. Japan 36,692, July 1, 1920. An inverted bottle contg. HCl with inverted funnel is placed on the bath.  $H_2$  generated in the bath enters the bottle through the funnel and displaces HCl into the bath.

## 5—PHOTOGRAPHY

LOUIS DERR

Structure of the photographic image. C. F. K. MEES. *J. Frank. Inst.* 191, 631-50 (1921).—The relationship between the size, number, and arrangement of the particles of Ag halide in the photographic emulsion and the graininess of the image are discussed. Other factors which modify the image are also considered. Sections are devoted to the unexposed emulsion, the developed image, the graininess of the image, and the sharpness of images. JOSEPH S. HEPBURN

Reduction of sensitiveness of silver bromide by amidol and allied substances. LÜPPO-CRAMER. *Phot. Ind.* 1920, 505-6.—Using 1/2000 solns., amidol reduces the sensitiveness to 1/200, triaminotoluene to 1/600, triaminobenzene and triaminophenol to 1/60-1/70, diaminoresorcinol less still, and metol to 1/4. Plates bathed with erythrosin still retain some color-sensitiveness after treatment with amidol, so that the method of development previously recommended, using a bright yellow light (*C. A.* 15, 2394), is not applicable to such plates. J. S. C. I.

Action of developing solutions on sensitiveness of silver bromide. LÜPPO-CRAMER. *Phot. Ind.* 1920, 604-8.—Alk. solns. of quinol, metol, and edinol free from sulfite desensitize considerably, though less than amidol (cf. preceding abst.), pyrogallol solns. desensitize much less, and *p*-aminophenol, glycine, and catechol hardly at all. Plain aq. solns. behave similarly if allowed to oxidize. Sulfite in as low concn. as 3.5% almost completely prevents the desensitizing action, but the effect is only temporary, desensitizing starting as soon as the oxidation of the sulfite allows formation of developer oxidation products. The effect is, therefore, due to interaction between the Ag salt and the oxidation product. Quant. measurements were made with quinol (*i. e.*, with its



oxidation product, quinone), and with metol. The fact that strongly oxidized amidol soln. is less effective than a fresh, slightly oxidized soln. is explained as due to the existence in the former case of oxidized substance in colloidal condition and incapable of penetrating the film. The treatment with oxidized metol, and to a less extent with oxidized quinol, increased both the printing-out speed to daylight and the resulting density of the image. Quinone mixed with quinol has a stronger desensitizing action than quinone alone, but mixed with quinol developer or metol-quinol developer green solns. are produced, and there is no desensitizing. J. C. S. I.

**Desensitizing—an oxidation process.** LÜPPO-CRAMER, *Phot. Ind.* 1921, 259.—It is suggested that the action of desensitizers is an oxidizing action on the latent image, which is bleached if exposed to light in the presence of certain desensitizing dyes. Plates which are uniformly exposed, then dyed and then exposed to a subject, give reversed images showing definite sensitiveness. If AgBr diapositive plates are exposed, converted into iodide, and then stained, the AgI complex is strongly color-sensitive. J. C. S. I.

**Desensitizers.** E. KÖNIG AND LÜPPO-CRAMER. *Phot. Rundschau* 1921, 37-8.—Dyestuffs of other classes than the safranine group (cf. C. A. 15, 808), contg. several amino groups, e. g., chrysoidine, are somewhat active as desensitizers; those with only one amino group, such as Congo red, are quite without action. The replacement of the H of the amino group by methyl has no effect on the desensitizing power. J. C. S. I.

**Desensitizing autochromes.** C. ADRIEN. *Bull. soc. franc. phot.* [3] 8, 110-2 (1921).—Phenosafranine, already used as a desensitizer in developing ordinary plates, is highly successful for autochromes. The colors are unchanged, and the staining of the plate due to the dye disappears in the acid permanganate bath. The appearing of the image and its development may be followed by the eye. Development is retarded about one-third. L. DERR

**Photographic plates for the extreme ultra-violet.** J. DUCLAUX AND P. JEANTRE. *J. phys. radium* 2, 156-9 (1921).—Ordinary plates are soaked 4 hrs. in 10% H<sub>2</sub>SO<sub>4</sub> (66%), at an av. temp. of 25°, a little higher at first and lower at the end. They are then withdrawn and washed 30 min. in a very gentle current of water. Drying is rapid because of the small amt. of gelatin left on the plate. The film is uniform and very sensitive to the extreme ultra-violet, but is very tender, and just before development may be protected by flowing with collodion, which does not affect development if the plate is immersed in the developer before the collodion is dry. Because of the removal of most of the absorbing gelatin, the sensitiveness to these rays is increased at least 100-fold. Twice this increase was obtained by coating the film of an ordinary plate with a non-aqueous blue-fluorescing substance; esculin in glycerol or simply a few drops of any fluorescing machine oil may be rubbed over the plate. Before development the plate must be cleaned with ether and alc. Excellent results were obtained. L. DERR

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SPÖRL, HANS: *Praktische Rezeptsammlung für Fach- und Liebhaber-Photographien*. 6th Ed. revised and enlarged. Leipzig: Ed. Liesegang's Verlag M. Eger. M 15, bound M 18. For review see *Papier-Ztg.* 46, 2246 (1921).

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**Photography.** L. RATIER. *Brit.* 148,462, July 10, 1920. In a modification of the ozobrome process, the alum is omitted from the bath in which the C paper is immersed, and the paper is impregnated with the reagents of the ozobromic bath, without alum, and kept until required, being immersed in H<sub>2</sub>O or in a soln. of one of the constituents of the ozobromic bath prior to use. One or more reagents, e. g., the dichromate, may be omitted from the bath and the paper subsequently treated with this reagent or with other reagents not previously included. For the paper, gelatin can be replaced



by albumin, gum or other mucilaginous substances, while the pigments can be constituted by inert coloring matter in powdered form other than C. A formula is specified containing amber, glue, gelatin, soap, sugar, coloring matter,  $\text{KBr}$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ , and  $\text{H}_2\text{O}$ . The silver print can be reinforced or weakened in a bath containing formol, "hydroxyl," chrome alum, and  $\text{H}_2\text{O}$ .

**Photography.** RIKIO NISHINO. Japan 36,473, July, 16, 1920. The exposed and developed film is washed with  $\text{H}_2\text{O}$  and immersed in an alc. soln. of I until the surface of the film becomes white. It is then immersed in KI soln. ( $3\text{KI}$  in  $28\text{H}_2\text{O}$ ) for 3 min. then in  $\text{HgCl}_2$  soln. ( $1.8\text{HgCl}_2$  in  $28\text{H}_2\text{O}$ ) for 5 min., producing  $\text{HgKI}$ , and washed with  $\text{H}_2\text{O}$  during 1 hr. The film is tinged with yellow color.

**Color photography.** F. E. IVES. U. S. 1,376,940, May 3. Color photographs or motion picture films are formed of two blended or blendable images, one consisting of a dichroic image showing two secondaries and the other showing the third secondary.

**Photographic transfer printing plate.** R. JOHN. U. S. 1,374,853, Apr. 12. A photographic record of lights and shades adapted for use as a transfer printing plate is formed by hardening portions of emulsion adjacent the light-affected sensitive content of a photographic emulsion with a developing reagent such as pyrogallie acid, together with a neutralizing agent such as  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_3$  in sufficient amt. to control the action of the hardening agent without entirely neutralizing it.

**Photosensitizing dyes.** E. Q. ADAMS and H. L. HALLER. U. S. 1,374,871, Apr. 12; cf. C. A. 14, 1793. Lepidine methiodide or ethiodide or *p*-tolulepidine methiodide when treated in  $\text{MeOH}$  soln. with strong bases such as  $\text{Na}$  or  $\text{K}$  methylate or ethylate or hydroxide or  $\text{Ag}_2\text{O}$  and heated yields dyes of the isocyanine type adapted for use with photosensitive compus. U. S., 1,374,872 relates to similar dyes prepd. with the additional use of  $\text{CH}_2\text{O}$  or  $\text{CHCl}_3$  to promote the dye-forming reaction. The characteristic absorption max. of this class of dyes is about  $7000\text{Å}$  and their sensitization max. approx.  $7400\text{Å}$ .

## 6—INORGANIC CHEMISTRY

### II. I. SCHLESINGER

Some questions of nomenclature in inorganic chemistry. ARTHUR ROSENHEIM. Berlin. *Z. angew. Chem.* 33, Aufsatzteil, 78 9(1920).—R. agrees with Stock (C. A. 14, 1941) that reform is needed but criticizes the latter's use of figures to indicate valence in names, e. g., iron (2) sulfate for ferrous sulfate, on the ground that it is confusing and based on hypothesis; R. and Koppel use names which are merely written-out formulas, as 2-iron-3-oxide for ferric oxide.—Remarks on the foregoing. ALFRED STOCK. Berlin. *Ibid* 79–80.—Reply to Rosenheim.

AUSTIN M. PATTERSON

A system of molybdates. S. POSTERNAK. *Compt. rend.* 172, 597–9(1921); cf. C. A. 15, 810, 993.—Forsen (C. A. 15, 2042) expresses the compn. of all complex molybdates in terms of more or less satd. salts of the 2 acids  $\text{Mo}_6\text{O}_{21}\text{H}_2$  and  $\text{Mo}_6\text{O}_{13}\text{H}_4$ . P. believes that it is impossible to express the penta-, hepta-, undeca-, or tridecamolybdates in this manner. He shows, that, while the results of different investigators are fairly concordant, the water content of Forsen's proposed mixed salt differs from the observed results. The acid reaction to phenolphthalein of polymolybdates, which Forsen attributes to incomplete neutralization of these polybasic acids, is really due to the formation of higher complexes in acid soln. and the decompn. of these complexes on the addition of alkali.

F. E. BROWN

Preparation of aluminium carbide and of marsh gas. O. OHMANN. *Z. physik. chem. Unterricht* 34, 76–77(1921).—A mixt. of 4 g. Al filings and a pinch of  $\text{KClO}_3$



† Fe is ignited in an atm. of  $\text{CO}_2$ . The operation is carried out in a large battery jar the bottom of which is covered with three pads of asbestos. The ignition is started by touching the  $\text{KClO}_3 + \text{Fe}$  with a glowing wire, and the stream of  $\text{CO}_2$  is played over the aluminium powder. The  $\text{CO}_2$  is reduced and the carbon reacts with part of the aluminium to form  $\text{Al}_4\text{C}_3$ . The powder is finely ground in mortar and when treated with water (heating gently) liberates methane  $\rightarrow \text{Al}_4\text{C}_3 + 6\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2\text{O}_3$ . About 70 cc. of  $\text{CH}_4$  can thus be obtained. S. MORGULIS

Solubility of graphite in molten iron (RUEP, BIREN) 9.

ASCH, W. AND ASCH, O.: The Silicates in Chemistry and Commerce. London: Constable and Co., Ltd. \$6.75. For review see *Eastman Kodak Co. Abst. Bull.* 6, 331(1920).

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

**Bromometric determination of salicylic acid.** I. M. KOLTHOFF. Utrecht. *Pharm. Weekblad* 58, 699-702(1921).—A study of the detn. of salicylic acid with Br (Fresenius and Grünhut, *Z. anal. Chem.* 38, 298 (1899)) showed that the amt. of excess of Br has little influence, but that the degree of acidity is very important. Addition of 2-6 cc. of 4 N HCl per 50 cc. of titration soln. gives a suitable acidity. To det. very small amts. of salicylic acid or salicylates (0.012-0.008 N), add to 25 cc. of sample 25 cc. of 0.1 N  $\text{KBrO}_3$ , 1 g. of NaBr and 5 cc. (not more) of 4 N HCl. Let stand 5-10 min. in a stoppered flask, add quickly 5 cc. of N KI and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Starch should be added till near the end of the titration.

JULIAN F. SMITH

**Sodium salicylate as a reagent for manganese, even in presence of zinc.** C. VAN ZIJP. Buitenzorg. *Pharm. Weekblad* 58, 698(1921).—Salts of Mn give long, pale-green needles in star-shaped clusters when treated with Na salicylate and  $\text{NH}_3$ . If Zn is present, ppt. with Na salicylate on a microscope slide, expose to  $\text{NH}_3$  till the ppt. dissolves, and place under the microscope. Greenish brown needles soon appear around the edge of the drop if Mn is present.

JULIAN F. SMITH

**Oxidimetric determination of manganese in hydrofluoric acid solution.** I. JOSEF HOLLUTA AND JOSEF OBRIST. Deut. Tech. Hochschule, Brunn. *Monatsh.* 41, 555-71 (1921).—The reaction  $\text{MnO}_4^- + 3\text{Mn}^{++} + 8\text{H}^+ = 5\text{Mn}^{+++} + 4\text{H}_2\text{O}$  proceeds in the presence of an excess of  $\text{F}^-$  with the quant. formation of a complex ion  $\text{MnF}_6^{3-}$ . This fact is made the basis of an oxidimetric detn. of Mn, in which the slightest excess of  $\text{KMnO}_4$  in the yellowish red liquid at the end of the reaction is detected by means of a small pocket spectroscope. The neutral or slightly acid Mn soln. (not over 0.2 g. Mn) is dild. in a 850-1000 cc. erlenmeyer to 300 cc., 5-10 cc.  $\text{H}_2\text{SO}_4$  (1:7) and 5 g.  $\text{NH}_4\text{F}$  are added and the mixt. is titrated with 0.1 N  $\text{KMnO}_4$  in the cold, with the flask so arranged that the contents can be viewed in front of an electric lamp by the spectroscope. At first the  $\text{KMnO}_4$  is decolorized at once and the spectroscope is not used until the liquid begins to show a yellowish red color (after  $\frac{1}{2}$  of the  $\text{KMnO}_4$  has been added). When the absorption lines from a drop remain more than 5 minutes, the titration is ended. The lines to be observed are the 2nd and 3rd (547.3 and 522.8  $\mu$ ). The following conditions must be observed: excess of  $\text{F}^-$ , low  $\text{H}^+$  concn., low temp. and large dila. The presence of large amts. of  $\text{Fe}^{+++}$  and of  $\text{Cl}^-$  and  $\text{NO}_3^-$  do not disturb the quant. nature of the reaction. C. J. WEST

**Sodium salicylate as a reagent for aluminium.** C. VAN ZIJP. Buitenzorg. *Pharm. Weekblad* 58, 694-8(1921).—A soln. of Na salicylate gives with Al salts a ppt. of fine



needles which cluster into spheroids. CsCl favors the crystn. The crystals are sol. in presence of excess Na salicylate. Salts of Fe and Cr also give ppts., but they are distinguishable by their color and cryst. form. Small amts. of Fe may be detected in Al by the brown color they impart to the crystals. The ppt. obtained from Al can be easily identified under the microscope. Treatment with  $\text{NH}_3$  aids in the differentiation from Fe and Cr.

JULIAN F. SMITH

**Rapid analysis of commercial aluminium.** GIORGIO MALVANO. *Giorn. chim. ind. applicata* 3, 102-3(1921).—The methods at present in use for the detn. of Al are very long and not very precise. The results are generally high. M. proposes to det. the amt. of Al for com. purposes by difference after detg. Si, Fe and Cu. C and Na occur generally in such small amounts as to be negligible. His method is as follows: Dissolve 1 g. com. Al in a porcelain dish with 30-31 cc. of an oxidizing mixt. composed of 100 cc. 1.42  $\text{HNO}_3$ , 100 cc. 1.2  $\text{HCl}$ , and 600 cc. 25%  $\text{H}_2\text{SO}_4$  in the cold (the reaction produces great heating), and towards the end of the reaction at a moderate temp. Then evap. upon the sand bath until white fumes of  $\text{SO}_3$  are given off, which are allowed to continue for several min. After cooling, take up with 100 cc. boiling  $\text{H}_2\text{O}$  containing 3-4 cc. 1.84  $\text{H}_2\text{SO}_4$ , bring to boil for a few min. until the Al is completely dissolved, and filter. Subject the filtrate to electrolysis at the ordinary temp. with a current of 2.5-3 v. and 1 amp. Within 1 hr. with a rotating cathode, and within 2 hrs. at the most with a fixed cathode, the Cu is completely deposited, and is generally shining and unoxidized if the operation has not been pushed too hard. Det. the Fe in the  $\text{H}_2\text{SO}_4$  soln. free of Cu by means of  $\text{KMnO}_4$ , after having reduced the Fe as far as possible with pure Zn (1 g. is more than sufficient) and a few cc. concd.  $\text{H}_2\text{SO}_4$ .  $\text{SiO}_2$  remains upon the filter from the earlier filtration together with a little graphitic Si and sometimes traces of  $\text{Al}_2\text{O}_3$ . Calcine this filter residue before the blast and weigh. Ordinarily the wt., calcd. as  $\text{SiO}_2$ , is sufficiently accurate, if the residue is treated with a few drops of concd.  $\text{H}_2\text{SO}_4$  and a few cc.  $\text{HF}$ , calcined and weighed again,  $\text{SiO}_2$  and hence Si being obtained by the difference between the weighings before and after treatment. For exact work, fuse the residue upon the filter with 1 g.  $\text{Na}_2\text{CO}_3$  to change the graphitic Si to  $\text{SiO}_2$ . Treat the fused mass with acidulated  $\text{H}_2\text{O}$ , dry, ignite, and proceed as above. Ordinarily the method is sufficiently accurate, and with a rotating cathode requires 2-3 hrs., and not more than half a day with use of a fixed cathode. The method is not complete for special aluminiums which show (on previous qual. tests) appreciable amts. of Pb, Sn or Zn. These must be detd. by the usual methods.

ROBERT S. POSMONTIER

**Notes on the determination of aluminium in its salts.** ALFRED TINGLE. *J. Ind. Eng. Chem.* 13, 420-2(1921).—Four methods were tested for the titrimetric detn. of Al. The most suitable method is one said to have been adopted in the German Pharmacopoeia. To 100 cc. of the boiling soln. add dropwise 5 cc. of satd.  $\text{BaCl}_2$  soln. and 4 or 5 drops of 0.1% phenolphthalein soln. and titrate the hot soln. with  $\text{NaOH}$  which is not over 0.5 N.

W. T. H.

**The determination of cobalt and nickel in cobalt steels.** G. E. F. LUNDELL AND J. I. HOFFMAN. U. S. Bur. Standards. *J. Ind. Eng. Chem.* 13, 540-3(1921).—After the removal of the  $\text{SiO}_2$  and  $\text{WO}_3$  from the oxidized  $\text{HCl}$  soln. of the steel, Fe and Mo are removed for the most part by treatment with ether. The soln. is then evapd. with  $\text{H}_2\text{SO}_4$  and oxidized by treatment with  $\text{K}_2\text{S}_2\text{O}_8$ . The dild. soln. is poured into hot  $\text{NaOH}$  soln. and the ppt. dissolved by means of  $\text{H}_2\text{SO}_4$  and  $\text{NaHSO}_3$ . Cu is removed by treatment with  $\text{H}_2\text{S}$  and the residual Fe by double pptn. with  $\text{NH}_4\text{OH}$ . The Ni and Co are then deposited electrolytically and, after dissolving the weighed deposit, the Ni is pptd. as dimethylglyoxime salt. Provision is made for the recovery of Ni and Co from the  $\text{SiO}_2$  ppt. and from the electrolyzed bath as well as for the accurate detn. of Cr, V, Cu, and Mn in the same portion.

W. T. H.



**Improved Denigès test for the detection and determination of methanol in the presence of ethyl alcohol.** ROBERT M. CHAPIN. U. S. Dept. Agr. *J. Ind. Eng. Chem.* **13**, 543-5(1921).—The test depends upon the oxidation of MeOH to HCHO and testing for the latter with the Schiff-Elvove reagent. In the new procedure, 0.2 cc. of 85%  $\text{H}_2\text{PO}_4$  is used instead of 0.2 cc. of concd.  $\text{H}_2\text{SO}_4$  and the oxidation with  $\text{KMnO}_4$  is given 30 min. instead of 3 min. because the max. yield of HCHO is obtained by slow oxidation with low hydron concn. Methods of procedure are given to prevent interference of carbohydrates, glycerol, formic and acetic acids, formaldehyde, terpenes, phenol, fusel oil and acetone. W. T. H.

**The determination of small amounts of lead in brass.** FRANCIS W. GLAZE. *J. Ind. Eng. Chem.* **13**, 553-4(1921).—The usual method of depositing  $\text{PbO}_2$  from  $\text{HNO}_3$  solns. has been found to give good results with samples of low Pb content. A current of  $\text{ND}_{100} = 1.5$  amp. at 2.9-3 volts is recommended. A sample of 8.643 g. is taken and the electrolyte contains 5 cc. of concd.  $\text{HNO}_3$  in about 100 cc. of soln. W. T. H.

**Separation of silicon, tin, titanium and zirconium from one another by the sodium carbonate method.** PAUL WENGER AND JULES MOREL. *Ann. chim. anal. chim. app.* **3**, 139-42(1921).—The oxides of these 4 elements were fused singly, in pairs and all together with  $\text{Na}_2\text{CO}_3$ . The mixts. were heated  $1\frac{1}{2}$  hrs. over the Bunsen flame and an equal time over the blast. After allowing the melt to cool below  $100^\circ$ , the crucible was filled  $\frac{1}{4}$  full of water which was heated to boiling in the crucible. In this way the melt was easily detached from the crucible. Silicon was converted into sodium silicate, entirely soluble in water. Stannic oxide was partially converted into sodium stannate but a considerable part was left in the insol. residue. The oxides of Ti and Zr did not form water-sol. Na compds. By careful fusion with  $\text{KHSO}_4$  Zr and Ti oxides can be made sol. in water but  $\text{SnO}_2$  is scarcely affected. A fairly accurate separation can be made as follows: Fuse the oxides of these 4 metals with 6 times as much  $\text{Na}_2\text{CO}_3$ , treat the melt with water and filter. Evaporate the filtrate with  $\text{HNO}_3$  and, after the dehydration of the silica, treat with  $\text{HNO}_3$  and filter off the silica and tin oxide. Det. the wt. of the former by treatment with  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  in the usual way. In the same crucible contg. some  $\text{SnO}_2$ , calcine the residue of Ti, Zr, Sn, oxides obtained from the  $\text{Na}_2\text{CO}_3$  fusion, weigh and fuse with 15 times as much  $\text{KHSO}_4$ . Dissolve the melt in water and  $\text{HNO}_3$ , filter and weigh the residual  $\text{SnO}_2$  after proper ignition. Neutralize the acid soln. very carefully and ppt. the Zr by means of  $\text{H}_2\text{O}_2$ . In the filtrate ppt. the Ti by means of  $\text{NH}_4\text{OH}$ . W. T. H.

**Further experiences with the determination of copper by means of potassium thiocyanate (in the determination of invert sugar).** G. BRUHNS. *Centr. Zuckerind.* **29**, 34-5, 85-8(1920).—B. has again found that 10 g. of cane sugar reduces 37-39 mg. of Cu, using not only gravimetric methods but also that of Bruhns (cf. C. A. **15**, 351). Therefore, the reducing table based on this method is correct in its entirety. The different values obtained by various investigators (11-45 mg. Cu) can be attributed to the difficulties encountered in the gravimetric detn., and also to the insufficiently pure Seignette salt used. This latter factor is especially significant if the solns. to be tested bind some of the iodine. In any case the titer of the 20 cc. of Cu soln. should be made as carefully as and similarly to the actual detn. (*loc. cit.*) Distd. water should be used, the thiosulfate must be pure and give a clear aq. soln. on the addition of 1 cc. of  $\text{N NaOH}$  per l. and under const. temp. conditions remain unchanged. The starch used should be of the finest quality, giving clear solns. The calcn. of the amt. of thiosulfate used to Cu by means of Herzfeld's, Baumann's or Schrefeld's tables gives values practically identical with those obtained by use of Bruhns' tables. JOHN M. KRISO.

**$\beta, \beta'$ -Diiododiethyl sulfide and its application to the detection and determination of pyrite.** V. GRIGNARD, G. RIVAT AND G. SCATCHARD. *Ann. chim.* **15**, 118(1921).



When 1 g. of  $(C_2H_5Cl)_2S$  (A) in 10 g. of glacial AcOH is heated with 6–7 cc. of 67% HI at 50–70°, a yellowish oil is deposited which solidifies on cooling to a cryst. mass of  $(C_2H_5I)_2S$ , m. 62° after recrystg. from EtOH, sol. in EtOH and AcOH, very sol. in Et<sub>2</sub>O, insol. in H<sub>2</sub>O and stable in the light when pure. The Cl atoms of A are much more reactive than those of EtCl, or PhCH<sub>2</sub>Cl, and even with 7% HI the reaction is complete in a few min. A 6% soln. of NaI.2H<sub>2</sub>O apparently reacted more rapidly than 7% HI. Thiodiglycol,  $(C_2H_4OH)_2S$ , (B), reacts similarly. For quant. detns., weigh 0.7–0.8 g. of B into a 50-cc. flask, add 5 cc. of 54–55% HI, and heat for 15–20 mins. at 70–75°, cool, filter, wash with H<sub>2</sub>O until neutral, and titrate the free I in the filtrate and washings with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, then titrate the excess HI with N NaOH. If A is the vol. of N NaOH used, and B the vol. of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, while A<sub>0</sub> and B<sub>0</sub> are the corresponding values from a blank detn., the amt. of B present is  $61 [A_0 - A - (B - B_0)/20]$  mg., with a max. negative error of 5%. The free I is probably due to a slight hydrogenation. For the detn. of A, whether made from B or from S chlorides, about 1 g. (wt. = P) of sample is introduced into a small flask with an air condenser, with 15 cc. of glacial AcOH and exactly 5 cc. of 54% HI, and the whole heated 15 mins. at 70°. After cooling, the contents of the flask are washed into a 500-cc. volumetric flask containing exactly 100 cc. of CCl<sub>4</sub> and about 200 cc. of H<sub>2</sub>O. After soln. of the ppt. the flask is filled to the mark with H<sub>2</sub>O, shaken well, and 50 cc. of the aq. layer treated with 10 cc. of 10% NaNO<sub>2</sub>. The liberated I is extd. once with 20 cc. and 4 times with 10 cc. of CCl<sub>4</sub>, the united CCl<sub>4</sub> solns. washed once with 100 cc. of H<sub>2</sub>O, and the I titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the vol. used being A<sub>1</sub> cc. The CCl<sub>4</sub> soln. in the 500-cc. flask is then sepd. carefully, the aq. soln. washed with a little CCl<sub>4</sub>, which is added to the main soln., and the combined CCl<sub>4</sub> solns. are titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the vol. consumed being A<sub>2</sub> cc. A blank detn. of the total I in 5 cc. of the HI soln. used is made, using 15 cc. of AcOH and 10 cc. of 10% NaNO<sub>2</sub>, the 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> consumed being A<sub>3</sub> cc. The % of A in the sample is then  $0.82/P [10A_0 + 1.5 - (8A_1 + A_2)]$ . Derivs. of A containing additional Cl undergo incomplete reaction with HI and hence titrate partially, 15% of those superchlorinated compds. increasing the apparent % of A by 2.5–3.0%. For detecting A in aq. solns. obtained by washing earth, food, metals, wood, clothing, etc. with H<sub>2</sub>O or by passing contaminated air through H<sub>2</sub>O, 1 cc. of 30% NaI.2H<sub>2</sub>O soln. is added to 4 cc. of the aq. soln. and heated to 60–70° for a few seconds. A turbidity appears on cooling, which will indicate a concn. of 0.0375 g. per l. For work in the field, where heat may be unobtainable, the NaI soln. is modified as follows: To 50 g. of the 30% NaI soln. add 30 drops of 7.5 CuSO<sub>4</sub> soln. The ppt. formed soon dissolves, giving a clear soln. colored by I. Any turbidity is filtered off after several hrs., after which the reagent keeps indefinitely if protected from light. At 21°, a concn. of 0.0025 g. of A per l. gave a turbidity in 3.6 mins., while 0.025 g. per l. gave a visible reaction in 7.7 mins. If contaminated air is passed through the reagent, the turbidity soon assumes cryst. form and is difficult to see. This is avoided by using a reagent containing 20 g. NaI.2H<sub>2</sub>O, 1.64 g. CuSO<sub>4</sub>, and 2 cc. of 35% gum arabic soln. in 200 cc., the gum arabic maintaining the colloidal nature of the iodized A. The reaction is not given by B unless the concn. reaches 1%, nor by trichloromethyl chloroformate, chloropicrin, chlorinated Me and Et sulfates, acrolein, chlorinated phenylarsines, or PhCH<sub>2</sub>Br. Dichloro- or dibromoethylarsines give a permanent turbidity in concns. of 40 g. per l. Chlorinated phenylcarbamine gives a turbidity when the concn. is 20 times the soly. of A.

M. R. SCHMIDT

**Detection of methanol in spirits.** F. HAHN. *Pharm. Ztg.* 66, 134–5 (1921); *J. Chem. Soc.* 120, II, 281.—The fact that the presence of HCl interferes with the sensitivity of the morphine-H<sub>2</sub>SO<sub>4</sub> reagent used for the detection of CH<sub>3</sub>O resulting from the oxidation of MeOH, as mentioned by Rabe, has been known for some time, for



which reason morphine sulfate, not the hydrochloride, should be used in prepg. the reagent. W. O. E.

Detection of methanol in spirits. F. RABE. *Pharm. Ztg.* 66, 135(1921); *J. Chem. Soc.* 120, II, 281.—A reply to Maue (*C. A.* 15, 1373); the author is quite aware that the resorcinol-sulfuric acid test is not new, but he recommended it as a useful confirmatory test for  $\text{CH}_3\text{O}$ . W. O. E.

Detection of methanol. G. MAUE. *Pharm. Ztg.* 66, 169(1921); *J. Chem. Soc.* 120, II, 281.—A reply to Rabe (cf. preceding abst.). Under definite conditions and in the presence of excess of  $\text{HCl}$ , the magenta- $\text{SO}_2$  acid reaction is characteristic of  $\text{CH}_3\text{O}$ . W. O. E.

Volumetric determination of oxalic acid. A. ABELMANN. *Ber. pharm. Ges.* 31, 130-1(1921); *J. Soc. Chem. Ind.* 40, 368A.—To the oxalic acid or oxalate soln. in a 100-cc. flask, add 30-40 drops of 5  $N$   $\text{HNO}_3$ , and a measured excess of 0.1  $N$   $\text{Hg}(\text{NO}_3)_2$  soln., contg. sufficient  $\text{HNO}_3$  to produce a clear soln.; then follow with about 50 cc. of satd.  $\text{KNO}_3$  soln. and sufficient  $\text{H}_2\text{O}$  to make 100 cc. Let stand for 15 min., filter, and titrate an aliquot of the filtrate with  $N$   $\text{NH}_4\text{CNS}$ , using ferric ammonium sulfate as indicator. W. O. E.

Interference of phosphates in the detection of manganese, and its avoidance. TH. SABALITSCHKA AND H. NIESEMAN. *Ber. pharm. Ges.* 31, 30-6(1921); *J. Chem. Soc.* 120, II, 278.—The failure to detect Mn in the presence of an excess of Ba or Sr phosphate, when the sepo. of  $\text{H}_3\text{PO}_4$  is conducted *via* Schmidt, is obviated by the following procedure: The ppt. obtained with  $\text{NH}_4$  sulfide is dissolved in 5%  $\text{HCl}$  and filtered from insol. Ni and Co sulfides. The soln. is then evapd. with 2-3 g. concd.  $\text{H}_2\text{SO}_4$ , and a like quantity of satd.  $\text{K}_2\text{SO}_4$  soln. until white fumes are evolved, any ferrous Fe being previously oxidized by  $\text{HNO}_3$ . The mixed sulfates obtained are extd. with alc. to remove  $\text{H}_2\text{SO}_4$  (small quantities of Mn and Zn sulfates and most of the Cr also pass into soln.). The residue insol. in alc. is extd. with dil.  $\text{HCl}$  and the insol. sulfates of Ba, Sr and Ca are filtered off. From the filtrate Fe, Al and Cr are pptd. with  $\text{NH}_3$ , and then the sulfides of Zn and Mn and  $\text{H}_3\text{PO}_4$  with  $\text{NH}_4$  sulfide. The final filtrate contains Ca and Mg. W. O. E.

Sodium acetate method for the separation of the bivalent metals from the trivalent metals in the ammonium sulfide group. TH. SABALITSCHKA. *Ber. pharm. Ges.* 31, 36-7(1921); *J. Chem. Soc.* 120, II, 278.—The Na acetate method described by Mareri (cf. *Boll. chim. farm.* 59, 385) for the sepn. of Fe, Al and Cr from Zn, Mn, etc., is useless in the presence of Cr, as this metal is pptd. not at all when alone, and only partly in the presence of Fe and Al. W. O. E.

Identification of acetaldehyde and formaldehyde in organic liquids and mixtures by means of new, extremely sensitive, color reactions. EMILIO PITTARELLI. *Arch. farm. sper.* 30, 148-60(1920); cf. *C. A.* 15, 1869.— $\text{AcH}$  may be detected by adding, to 25-30 cc. of the approx. neutral liquid to be tested, successively 5 to 6 drops of satd. (about 0.1  $N$ ) phenylhydrazine hydrochloride soln., satd. diazobenzenesulfonic acid, 25%  $\text{NaOH}$  soln., and 50%  $\text{MgSO}_4$  soln.; the last may be omitted if the color appears after addition of the alkali hydroxide. A crimson coloration results, this beginning to appear almost instantaneously, although the reaction is complete only after some mins.; with the  $\text{Mg}(\text{OH})_2$ , this yields a violet lake. In absence of either  $\text{AcH}$  or phenylhydrazine, only a yellow coloration is produced, this remaining unchanged by  $\text{CH}_2\text{O}$  or acetone. The reaction is capable of detecting 1 pt. of  $\text{AcH}$  in 350,000 pts. of soln., or 1 pt. of phenylhydrazine in 70,000 pts. of soln. To detect  $\text{CH}_2\text{O}$ , 25-30 cc. of the liquid under examn. are treated in order with 5 to 6 drops of satd. phenylhydrazine hydrochloride soln., 1% metol soln., 25%  $\text{NaOH}$  soln., and 50%  $\text{MgSO}_4$  soln.; here, too, the last may be omitted if it is unnecessary. In presence of  $\text{CH}_2\text{O}$  a blood-red



coloration is formed, this giving a blue lake with the  $Mg(OH)_2$ . The reaction is capable of detecting 1 part of  $CH_3O$  in 1,000,000 parts of soln., 1 part of phenylhydrazine in 250,000 pts. of soln., and 1 pt. of metol in 300,000 pts. of soln. The above reactions may be applied directly to org. liquids and mixts., such as urine, wine, milk, spirits, beer, foods, etc.

J. C. S.

**Detection of acetone by degradation to derivatives of formic acid.** EMILIO PIRELLI. *Polichinico* 27, 1047-9(1920).—Acetone is converted by Cl, Br, or I in strongly alk. soln. into  $CHCl_3$ , etc. Excess of free halogen is removed and the halide is detected by warming with phenol and subsequent heating with alkali hydroxide, by the carbylamine reaction, or by reduction to  $C_2H_2$  (with Zn and  $NH_4$  chlorides).

J. C. S.

**Use of the silent electric discharge for the detection of fire-damp and for gas analysis.** G. ERLWEIN AND H. BECKER. *Wiss. Veröffentlich. Siemens Konzern* 1, 71-5(1920).—Variations of current strength occur when  $CH_4$  is present in the air flowing through a Siemens  $O_2$  tube in which a const. p. d. is maintained. Such variations of current strength are obtained with gaseous mixts. in which chem. action can take place between the constituents. The presence of H or  $CH_4$  in air causes a considerable increase of current strength. The variations of current strength can be detected by means of a galvanometer of the thermo-elec. type. By employing an intensifier tube in conjunction with a relay, signals can be operated indicating the presence of certain gases. The variations of current strength may also be used to det. the concn. of the gas admitted with the air.

J. S. C. I.

**Technical gas analysis, based on the measurement of thermal conductivity.** M. MÖLLER. *Wiss. Veröffentlich. Siemens Konzern* 1, 147-53(1920).—A method of technical gas analysis, especially for the detn. of H,  $CO_2$ , and  $CH_4$ , is based on the difference in the respective thermal conds. of certain gases.  $CO$ , N, and O are not differentiated from one another by the method, which is based upon the different cooling effects experienced by two exactly similar heated wires contained resp. within one of two exactly similar very narrow cylindrical metal chambers and surrounded resp. by the gas to be investigated and a standard gas (cf. *C. A.* 14, 1500, 3029). Air, or the gas under investigation, freed from the impurities, may be used as standard gas. Convection effects are eliminated as far as possible. The two wires constitute two arms of a Wheatstone network in which a constant elec. current is maintained, and the galvanometer scale is calibrated so that the deflection gives directly the percentage of one constituent present. The method is applicable only to gases contg. known constituents. With a portable app. a detn. of H in air can be made in 2-3 secs. The method can be used for indicating and controlling the combustion in furnaces at a distance.

J. S. C. I.

**The determination of sulfur dioxide and sulfur trioxide in the gases from pyrite burners and in oleum.** A. SANDER. *Chem.-Ztg.* 45, 261-3(1921).—The methods commonly employed for the determination of  $SO_2$  and  $SO_3$  in the presence of one another usually involve 2 titrations with 2 different standard solns. The proposed method can be carried out with a simple apparatus and only 1 standard soln. The gas is aspirated into 10 cc. of 0.1 N NaOH dild. with 200 cc. of water. It is convenient to use for the absorption a vessel shaped like a Woulfe bottle with a stopcock at the bottom through which the soln. can be withdrawn. It is convenient also to aspirate the gas by allowing water to flow from a large bottle with stopcock at the bottom and connecting the mouth of this bottle with the absorption bottle. The middle hole of the latter is closed with a stopper during the absorption but opened when the liquid is withdrawn. The third hole of the Woulfe bottle is connected with the supply of gas. By measuring the vol. of water flowing from the aspiration, the vol. of gas is detd. The gas is aspirated until the NaOH soln., which at first is colored yellow by the addition of methyl orange, turns pink. This gives the NaOH necessary to form  $NaHSO_3$  and  $Na_2SO_3$  from the



$\text{SO}_2$  and  $\text{SO}_3$ . Then the neutral soln. is transferred to a flask and treated with  $\text{HgCl}_2$  soln. whereby the following reaction takes place,  $\text{NaHSO}_3 + \text{HgCl}_2 \rightarrow \text{HgCl}_2\text{NaSO}_3 + \text{HCl}$  and the liberated acid is titrated with  $\text{NaOH}$ , showing the  $\text{SO}_2$  content. In the analysis of oleum the dild. soln. is first titrated with  $\text{NaOH}$ , using methyl orange as indicator, and then treated with  $\text{HgCl}_2$  as just outlined. W. T. H.

**Method for rapid analysis of graphite.** G. B. TAYLOR AND W. A. SELVIG. U. S. Bur. of Mines, *Bull.* 112, 43-5 (1920).—The following method is used at the Pittsburgh Lab. of the U. S. Bur. of Mines: If much gang is present the sample is ground to pass through a 60-mesh sieve. Moisture is detd. by heating 1 g. in a weighed Pt or porcelain crucible,  $\frac{1}{8}$  in. deep by  $1\frac{1}{4}$  in. wide, for 1 hr. at  $105^\circ$ . The crucible is cooled in a desiccator over  $\text{H}_2\text{SO}_4$  and the loss of wt. noted. Volatile matter is detd. by heating the dry graphite for 3 mins. in a muffle furnace at  $800^\circ$ , cooling as before, and noting the loss of wt. Ash is detd. by heating the non-volatile residue at  $800^\circ$  until all the graphite is burned away. Graphitic carbon is taken as the difference between the sum of the percentages of moisture, ash, and volatile matter and 100. Graphitic carbon in an ore is detd. by heating 0.2-1.0 g. in a 100 cc. evapg. dish with 25 cc. of  $\text{HCl}$  (1:1) on a hot plate for 15 min., filtering the mixt. through ignited asbestos and washing the residue with hot water. The filter and residue are transferred to a porcelain or Pt boat, dried on a hot plate, transferred to a combustion tube (contg. fused  $\text{PbCrO}_4$  to retain any S present), and burned in a stream of  $\text{O}_2$ . The  $\text{CO}_2$  formed is passed into a weighed potash bulb contg. 30%  $\text{KOH}$  soln. and weighed. Graphitic carbon is detd. in a concentrate by placing 0.2-0.5 g. of the sample in a small Erlenmeyer flask, adding about 25 cc. of ether, corking loosely, and allowing to stand for  $\frac{1}{2}$  hr., shaking at intervals. The mixt. is filtered through ignited asbestos, the residue washed with alc. and distd. water, then treated with acid to remove carbonates, and the detn. continued as described for ores. J. S. C. I.

**Collection and examination of rock dust in mine air.** W. A. SELVIG, F. D. OSGOOD, AND A. C. FIEDLER. *Repts. of Investigations, Bureau of Mines* No. 2122, 7 pp. (1920).—Dust samples are obtained in connection with investigations regarding pulmonary disease by drawing a known quantity of mine air by means of a calibrated air pump through a glass tube 2' x  $\frac{1}{4}$ " in diam. The tube contains 100 g. sugar passing a 14-mesh screen and remaining on a 65-mesh sieve. The sugar is supported in the tube by means of two monel metal screens, the lower 20-mesh and the upper 70-mesh. The air is drawn through the sugar filter at the rate of 1 cu. ft. per min. and ordinarily 15 cu. ft. are aspirated. After collection, the sample is treated with formalin to prevent bacterial growths. The dust is detd. by a counting cell. The factor used in multiplying the av. number of dust particles in  $\frac{1}{4}$  of the field is 2,000,000. Results are reported to millions so the factor becomes 2. A blank is made on the sugar. All dust counts are reported in millions of dust particles per cu. m. of air. As few particles larger than 10 microns in diam. reach the lung the particles are reported as particles over 10 microns and under 10 microns. The hand sampling pump and its calibration are fully described, also the method of collecting the dust samples and the form of report. W. H. BOYNTON.

**Comparative examination of analytical methods applied to metallic alloys. I. Determination of manganese in pig.** F. GRAZIANI AND L. LORANA. *Giorn. chim. ind. applicata* 3, 148-52 (1921).—The methods examd. were the following: (a) gravimetric (1) as  $\text{Mn}_2\text{O}_3$ , (2) as  $\text{MnSO}_4$ , (3) as  $\text{Mn}_3\text{P}_2\text{O}_{11}$ ; (b) direct volumetric, (4) Volhard, (5) Volhard-Wolf-Schiffel-Donath, (6) Campredon, (7) Volhard-Wolff, (8) Cadet and Rodieq; (c) indirect volumetric, (9) Knorre, (10) Hampe-Likena, (Ford-Williams); (d) oxidation, (11) Reddrop and Ramage, (as  $\text{Bi}$  tetroxide), (12) Schneider (titrate with  $\text{As}_2\text{O}_3$ , also titrate with  $\text{H}_2\text{O}_2$ ), (13) Procter Smith (at  $50^\circ$ , also at  $80-90^\circ$ ), (14) colorimetric with  $\text{Bi}_2\text{O}_3$ , (15) Marshall and Walter colorimetric with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Samples of gray



plg of high, medium and low Mn content were made the basis for comparison of the methods. The authors drew the following conclusions: (1) The gravimetric methods are the most precise but are too long for ordinary use. (2) The best method for ordinary use is Volhard's. (3) Campredon's is a modification of Volhard's which shortens it considerably yet gives very good results. (4) Reddrop and Ramage's method is sufficiently exact, but a little too long. (5) Procter-Smith method is recommended for rapid controls as it gives sufficiently satisfactory results if followed out according to the procedure of G. and L.

ROBERT S. POSMONTIER

**Guanidine carbonate as a standard alkali.** A. H. DONN. *J. Soc. Chem. Ind.* **40**, 89-90 T(1921).—Guanidine carbonate,  $[\text{NH}:\text{C}(\text{NH}_2)_2]\cdot\text{H}_2\text{CO}_3$ , when prepd. from  $\text{CaCN}_2$  is very pure, contains no  $\text{H}_2\text{O}$  of crystn. and is not hygroscopic. It behaves as a mono-acidic base when titrated against acid with indicators such as methyl orange, Congo red and alizarin red. It is certainly accurate enough for use as a standard in routine work.

W. T. H.

**The determination of zinc by the potassium ferrocyanide method.** E. OLIVIER. *J. Soc. Chem. Ind.* **40**, 107-8 T(1921).—The so-called American method for detg. Zn in ores causes Cd and Mn to be reported as Zn. By the addition of  $\text{H}_2\text{O}_2$  to the ammoniacal soln. the Mn may be pptd. and the results are then similar to those obtained by the Schaffner or Vieille-Montagne method of  $\text{Na}_2\text{S}$  titration which, however, is preferred by O.

W. T. H.

**A method for the determination of the acidity of colored solutions.** J. L. LIZIUS. *Analyst* **46**, 194-5(1921).—Moisten the filter paper of a small Büchner funnel with a few drops of phenolphthalein soln. and drain by suction. To 10 cc. of the colored soln. add 0.1 N alkali until just alkaline, detg. the end-point by withdrawing a little of the soln. by means of a capillary tube, and touching the filter paper but returning most of the soln. back to the titration beaker. When the capillary tube test gives a pink color, draw the entire soln. through the Büchner funnel. The filter paper is left a pink color. Rinse the contents of the Büchner flask back into the beaker and add 0.05 cc. of 0.1 N acid. Add a drop or two of phenolphthalein soln. to the filter paper and again filter the entire soln. If the filter is not pink, the vol. of alkali already added is the correct value. If the filter paper is still pink, repeat the treatment with 0.5 cc. acid and make the corresponding deduction from the original vol. of alkali used. If the color of the soln. is adsorbed by the filter, this can be remedied by washing through the paper a drop or two of phenolphthalein soln. The method has been tested in the analysis of stout, and different operators checked within 0.1 cc. of 0.1 N alkali but the variance was 6 times as much when the titration was made in the usual way.

W. T. H.

**The Przibylla tartrate method for potassium.** E. BORSCH. *Kali* **14**, 275-80, 303-8, 358-61, 374-82(1920).—It is shown that the pptn. of K by tartaric acid, filtration, and titration of the excess of tartaric acid in the filtrate, is employable as a works method, provided that the accompanying material is not too variable in compn. Tables are usually given for salts of 80% or higher grades. For fertilizer salts of 20 to 40% grade special tables must be made to allow for deviations caused by the different content of the other salts present.

J. C. S.

**Analysis of potash alum.** A. HARVEY. *J. Soc. Leather Trades' Chem.* **4**, 219-20 (1920).—Codwise (C. A. **15**, 2047) stated that the presence of Fe impurities does not affect the result. H. does not agree. c.p. potash alum showed 100% purity by this method, but when the sample was mixed with known amts. of  $\text{FeSO}_4$ , theoretical results were not forthcoming. Further expl. evidence is cited to show that sol. Fe impurities and any  $\text{NH}_4$  salts present are included in the titration.

C. F. JAMESON

**Determination of organic carbon in bituminous limestones.** EMILIO SERNAGIOTTO. *Giorn. chim. ind. applicata* **3**, 153-4(1921).—The detn. of org. C in bituminous lime-



stones and in general in natural substances containing org. compds. presents considerable difficulties. The values obtained by direct combustion according to Liebig's method or by loss on calcination are generally uncertain and variable. The presence of  $H_2O$  that is eliminated only at high temps. and of inorg. carbonate are the principal sources of error. S. modifies the method of Corleis which is normally employed for the detn. of total C of steels. The app. consists of a Corleis flask covered with asbestos, and provided with a concentric condenser. The flask must be carefully washed before use with a  $H_2SO_4$  soln. of  $CrO_3$ , and then with  $H_2O$ . Connected with the flask on one side is a purifying tower filled with pieces of KOH. Connected with it on the other side in train are a  $H_2SO_4$  drying bottle, a short infusible tube filled with  $CuO$  and  $PbCrO_4$  and heated to nascent red during the operation, a tube of  $P_2O_5$ , and finally 2 absorption tubes (which are previously weighed), one containing soda-lime and the other  $P_2O_5$ . Weigh out in a tube the substance to be analyzed, using such a quantity of substance as will contain about 0.1 g. org. C (det. the % of extractable substance in the original material with  $CS_2$ , in case of bituminous minerals), pour it into the flask by means of a large funnel, adding in the same way about 30 cc. sirupy  $H_3PO_4$ , causing the latter to wash well the sides of the flask. Wash the sides then with a jet of  $H_2O$  and close the flask with a 2-holed rubber stopper. The  $H_3PO_4$  decomposes the carbonate. The  $CO_2$  set free is drawn out of the flask by 3 or 4 evacuations with a good water pump. Allow the flask each time to refill with air drawn through the KOH tower. Warm the flask gently during each evacuation. Test for complete elimination of  $CO_2$  from the flask by passing the air through a little baryta water. Put in position the condenser and  $H_2SO_4$  seal, connect the flask to the absorption train, and heat the  $CuO$  tube. Pour into the flask about 35 cc. of a 50% pure com.  $CrO_3$  soln. dild. to 200 cc. with 1.84  $H_2SO_4$ . (Boil the reaction mixt. before using for about  $\frac{1}{4}$  hr. and cool.) Heat the flask slowly to boiling, continue this for about 4 hrs., and proceed as in Corleis method for detg. C in steels.

ROBERT S. POSMONTIER

Quantitative microscopic determinations of chalcopyrite, chalcocite, bornite and pyrite in a porphyry ore. R. E. HEAD. *Repts. of Investigations, Bur. of Mines No. 2257*, 5 pp. (1921).—The work described was undertaken to det. the relative amts. of these minerals in various portions of dressed ore. The samples were carefully panned by hand and then classified into 6 sizes. Sealing wax was melted and poured into a cardboard mold with a bottom. The wax was kept molten and about 4 g. of crushed ore were stirred into it. The cold, wax briquets were polished and the no. of grains of each constituent was counted under the microscope; in this way a fairly accurate estimation was made of the percentage composition. Such information could not have been obtained by ordinary chem. analysis. In the ore examined, chalcopyrite proved to be the predominating mineral but the greater part of the Cu was carried by chalcocite.

W. T. HALL

The detection of mercury as cuprous mercuric iodide. P. ARTMANN. *Z. anal. Chem.* 60, 81-88 (1921).—Statements in the literature concerning the delicacy of Behren's iodide test for Hg are conflicting. A. has found the test capable of detecting 1 pt. of Hg in 10,000 of water. In studying the test with the hope of making it more sensitive, it was assumed that the presence of an excess of insol.  $Cu_2I_2$  could do no harm and on trying the effect of freshly pptd.  $Cu_2I_2$ , it was found that  $Hg^{++}$  reacted with it and formed dark-red, less sol.  $Cu_2HgI_4$ , which is the basis of a more sensitive test for Hg. The reaction can be performed on a microscope slide and serves to detect 0.00006 mg. of Hg but when test paper is used the test is twice as sensitive. To carry out the test, spread a thin layer of freshly pptd. and washed  $Cu_2I_2$  upon filter paper, dry and add a drop of the soln. to be tested. A reddish spot shows the presence of Hg. The soln. tested should not be too strongly acid or contain substances which are reduced by  $Cu_2I_2$ .



The presence of Cu, Cd, trivalent Sb, quadrivalent Sn, Zn and even Pb does not interfere with the test but if large quantities of Bi are present, black BiI<sub>3</sub> may obscure the red spot.

W. T. H.

Gases in aluminium furnaces and their analysis (ANONSON, CAPPS) 9. Point discharge in nitrogen (PIRANI, LAX) 2. Equilibria of hydrofluosilicic acid (HUDLESTON BASSETT) 2.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

**Ullmannite from St. Andreasberg, Harz.** K. MIELEITNER. *Munich. Z. Kryst.* 56, 105-7(1921).—Specimens of shale from the Ag mine show in crevices cleavable calcite, quartz, natrolite, proustite, galenite, breithauptite and small crystals of ullmannite. The last shows overgrowth relation with the breithauptite, but they can be distinguished by their colors, and qual. tests proved the identity of the ullmannite, (NiSSb). On heating in the closed tube this crackles, melts, and gives brown spots (orange when cold) on the glass. The crystals show in addition to the cube both a pyritohedron and the tetrahedron, with a tristetrahedron on opposing corners, thus establishing the symmetry, which had previously been in doubt, as tetartohedral. The modern theory of crystal structure having indicated that the presence of two different negative elements in the pyrite structure should lead to tetartohedrism, this is an interesting confirmation of the theory.

E. T. W.

**Cesarolite, a new mineral.** H. BUTYGENBACH AND C. GILLET. Separate from *Ann. soc. géol. Belgique, Bull.* 43, 239-41(1920).—The mineral was found in cavities in galenite at the Pb mine at Sidi-Amer-ben-Salem, Tunis, and is named after Prof. G. Césaro of Liège. It is spongy, friable, and coke-like in aspect, bas H. = 4.5 and sp. gr. 5.29. Analysis gave Pb 36.29, MnO 42.65, H<sub>2</sub>O 3.30, O 13.26, Fe 0.49, Al 0.79, other metals 0.36, Na<sub>2</sub>O 0.18, insol. 0.75, and undetd. 1.93%. Sb, As, Cu, Zn, and Ca are present in minor amts., but CO<sub>2</sub> and S are absent. This is suggested to correspond to a hydrous Pb manganate, H<sub>2</sub>PbMn<sub>2</sub>O<sub>5</sub> [but may well be a colloidal adsorption product. —ABSTR.].

W. F. FOSHAG

**Secondary rutile in the millstone grit.** H. W. GREENWOOD. *Naturalist* 1917, 244.—Grains of rutile have been formed by alteration of titaniferous biotite. E. T. W.

**Minerals from Slatia, Tunis.** H. BUTYGENBACH. *Bull. soc. franç. mineral.* 43, 24-67(1920).—A crystallographic description of fine crystals of cerussite, anglesite, etc. Colorless crystals of calcite enclose brown filaments, which, as shown by the following analysis, consist of a hydroxide of Fe and Al with the compn. 3Al<sub>2</sub>O<sub>3</sub>.3Fe<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O: CaO 53.44, Fe<sub>2</sub>O<sub>3</sub> 2.54, Al<sub>2</sub>O<sub>3</sub> 1.58, H<sub>2</sub>O 0.38, CO<sub>2</sub> 42.02, total 99.96. J. C. S.

**Calcite crystals with curved faces.** G. AMINOFF. *Geol. För. Forh.* 39, 664-70(1917).—Crystals from Clausthal show curved rhombobedron faces, which are indicated by their relations to be transition faces.

E. T. W.

**The aragonites of Spain.** PEDRO CASTRO-BAREA. *Trab. Mus. Nac. Cienc. Nat. Madrid Geol. ser.* No. 24, 112 pp.(1919); *Rev. géol.* 1, 223(1920).—This paper includes a discussion of the origin of aragonite, and notes the occurrence of Mg in some specimens. In the course of spectrographic study of the mineral, 3 new lines of Ca were observed.

E. T. W.

**The siderite in the shaly clay of the Bolognese and Romagnolo Apennines.** V. SIMONELLI. *Rend. accad. sci. inst. Bologna* 1917, 6; *Rev. géol.* 1, 294(1920).—Certain peculiar nodules are shown to be impure and altered siderite, analysis yielding FeO 35.32 and MnO 13.33%. It may be of value as an ore.

E. T. W.



**Augite from Nishigatake, Japan.** RYŌICHI ŌHASHI. *Mineralog. Mag.* 19, 173-80 (1921).—The crystals are 7-10 mm. in length, and olive green to black in color. Sp. gr. = 3.344 at 15.7°. The forms observed are (100), (010), (001), (110), (221), (101), (111), and (021). Twinning on (100) is very frequent. Etch figures produced by HF on the faces of the prism zone indicate holohedral symmetry.  $\alpha = 1.6859$ ;  $\beta = 1.6917$ ;  $\gamma = 1.7105$ ;  $2V = 58^\circ 25.3'$ . The av. of duplicate analyses shows:  $\text{SiO}_2$  51.37,  $\text{Al}_2\text{O}_3$  5.24,  $\text{Fe}_2\text{O}_3$  2.02,  $\text{FeO}$  2.96,  $\text{CaO}$  21.58,  $\text{MgO}$  16.94,  $\text{TiO}_2$  0.58%. Recalcn. reveals the augite to consist very largely (78.2%) of the diopside mol. The Etna augite differs from that of Nishigatake in possessing more  $\text{CaO}$  and  $\text{TiO}_2$  and less  $\text{MgO}$ . W. F. HUNT.

**Some minerals from Fuchsbau, Fichtelgebirge.** K. MIELEITNER. Munich. *Z. Kryst.* 56, 90-4 (1921).—The first-formed minerals in the granite quarries at this locality are orthoclase, quartz, albite and zinnwaldite. Upon these are topaz in fine crystals, tourmaline, and apatite. As coatings over all these minerals occur gibberite, pyrolusite, and occasionally limonite. Heated waters circulating through fissures have deposited autunite and torbernite, and have altered the granite into a red clay, which has the compn. of kaolinite, apparently owing its color to the presence of Mn; because of the instability of the color it is inferred that a manganic ( $\text{Mn}^{IV}$ ) compd. is represented.

E. T. W.

**Some minerals from Gregnitz, Fichtelgebirge.** K. MIELEITNER. Munich. *Z. Kryst.* 56, 94-6 (1921).—In addition to minerals such as described in preceding abstract, this locality has yielded good crystals of phenacite, apparently formed by alteration of primary beryl.

E. T. W.

**Minerals of Lazio. Melilite as inclusions in peperino.** F. MILLOSEVICH. *Atti accad. Lincei* [5] 30, i, 80-4 (1921).—The peperino used for the foundations of the Villa Volterra at Albano (Latium) was found to contain clear, bright crystals of melilite having the compn.:  $\text{SiO}_2$  41.07,  $\text{Al}_2\text{O}_3$  10.47,  $\text{Fe}_2\text{O}_3$  3.80,  $\text{CaO}$  33.92,  $\text{MgO}$  6.02,  $\text{Na}_2\text{O}$  3.25,  $\text{K}_2\text{O}$  1.04, sum 99.57%; and the constn.,  $\text{D}^{25}_D$  2.929,  $n_c = 1.45643$ . If, as Schaller considers (*C. A.* 10, 2185), melilites consist of isomorphous mixts. of sarcolite, a hypothetical soda-sarcolite, vehardenite, and äkermanite, the sample now described contains 27.5, 9.0, 15.0, and 48.5% resp., of these components.

J. C. S.

**Monazite in the millstone grit of Yorkshire.** A. GILLIGAN. *Naturalist* 1917, 87-8.—This mineral has been identified by its absorption spectrum among the grains of heavy minerals in the rock.

E. T. W.

**Cohaliferous epsomite at Parkerville.** EDWARD S. SIMPSON. *J. Proc. Roy. Soc. W. Australia* 6 (pt. 2), 88-92 (1920).—An efflorescence on a chloritic rock was found on analysis to have the compn.:  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  91.78,  $\text{CoSO}_4 \cdot x\text{H}_2\text{O}$  2.41,  $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$  1.31,  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$  0.30 and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  4.17%. The value of  $x$  for this epsomite is 5.7 (the theory being 7). The absence of Fe and Al is noteworthy, these elements having been pptd. from the solns. before they reached the point where the efflorescence deposited. The low  $\text{H}_2\text{O}$  content is attributable to partial loss on exposure to warm dry air, expts. on ordinary crystd.  $\text{MgSO}_4$  having shown that the  $\text{H}_2\text{O}$  varies widely with the humidity of the surrounding atm. No optical data could be obtained.

E. T. W.

**Meteorites which fell at Boguslavka, 220 kilometers north of Vladivostok.** HELGE BACKLUND. *Geol. For. Förh.* 39, 105 (1917).—Two meteorites which fell on Oct. 18, 1916 weigh 199 and 57 kg. respectively, being the largest irons ever seen to fall. They are cubic kamacites, and detn. of Ni showed 5.25%, the sp. gr. being 7.860, both figures very close to those of the Braunau iron.

E. T. W.

**The meteoric stones seen to fall near Crumlin, Co. Antrim, on September 13, 1902.** LAZARUS FLETCHER. *Chemical analysis.* G. T. PRIOR. *Mineralog. Mag.* 19, 149-62 (1921).—The Crumlin stone weighs 9 lbs. 5 1/2 oz. (4239 g.), and is 7 1/2 in. (185 mm.) long, 6 1/2 in. (160 mm.) wide and 3 1/2 in. (84 mm.) thick. It is fragmental, with



concave and convex surfaces, and is covered by a crust (0.5–1.0 mm. thick), formed during flight through the air. Sp. gr. = 3.55. The compn. of the sol. silicate corresponds to an olivine with the formula  $3\text{Mg}_2\text{SiO}_4\cdot\text{FeSiO}_4$ . The approx. mineral compn. of the meteorite deduced from chem. analyses shows: feldspar 10.38%; chromite 0.87; ilmenite? 0.32; apatite? 0.59; pyroxene 30.15; olivine 43.67; nickel-iron 8.98; troilite 5.25%. The Crundin meteorite can therefore be classed as a gray hypersthene to bronzite chondrite containing 9% Ni-Fe, in which the ratio of Fe:Ni is about 7.

W. F. HUNT

**The South African meteorites Mount Ayliff and Simondium, and the chemical composition of the meteorites Adare and Ensisheim.** G. T. PRIOR. *Mineralog. Mag.* 19, 163-72 (1921).—METEORIC IRON OF MT. AYLIF, GRIQUALAND EAST: Its original weight was probably 30 lbs. Polished surfaces show large (up to 3 cm.) nodules of graphite and troilite. A striking feature is the cohenite, plates of which are so regularly distributed in lines parallel to the faces of an octahedron as to make the surface appear etched. The meteorite is a coarse octahedrite, the lamellas of kamacite being about 2 mm. wide. Taenite in very narrow bands bordering the kamacite is present in small amt., and plessite is almost absent. The result of analysis on the iron free from inclusions gave: Fe 91.73, Ni 6.59, Co 0.69, S 0.12, P 0.12, carbonaceous matter 0.51%. Negative tests were obtained for Cu, Pt, and Au. The residue examd. under the microscope showed no isotropic grains. SIMONIUM, LOWER PAARL, WESTERN CAPE PROVINCE: A former analysis of the "attracted" material was not very satisfactory owing to oxidized condition of the material. An analysis of purer material gave: insol. silicate 3.02, sol. silicate 2.65, Ni 23.79, Fe (+Co) by diff. 70.54%. In spite of its high Ni content it is placed with the mesosiderites because of the basaltic structure of the stony matter and the compn. of the feldspar, pyroxene, and olivine. ADARE: The approx. mineral compn. as deduced from analyses is: feldspar 7.52, chromite 0.87, apatite 0.63, bronzite (in which  $\text{MgO}:\text{FeO}=5$ ) 33.83, olivine (in which  $\text{MgO}:\text{FeO}=$ ) 32.64, nickel-iron (in which  $\text{Fe}:\text{Ni}=11$ ) 18.46, troilite 5.60%. ENSISEHEIM: feldspar 9.32, chromite 0.51, apatite 0.59, hypersthene (in which  $\text{MgO}:\text{FeO}=3$ ) 23.64, olivine (in which  $\text{MgO}:\text{FeO}=2\frac{1}{2}$ ) 55.03, nickel-iron (in which  $\text{Fe}:\text{Ni}=3\frac{1}{2}$ ) 3.29, troilite 6.59%. The analyses of both the Adare and Ensisheim meteorites afford additional support to the suggestion that in meteoric stones the ratio of MgO to FeO in the silicates varies directly with the ratio of Fe to Ni in the nickel-iron.

W. F. HUNT

**Etching iron meteorites.** OLIVER C. FARRINGTON. *Am. Mineral.* 5, 57-9 (1920).—New procedures are recommended, comprising holding the meteorite section by a magnet, and then dipping it into the etching liquid; lacquering nodules which need protection with "steel gloss"; and immersing the section after etching and washing in lime water to neutralize excess acid.

E. T. W.

**Microscopical detection of platinum and gold in the Siegerland "grauwacken."** H. SCHNEIDERHÖHN. *Metall u. Erz* 17, 511-4 (1920).—The rock is a medium-grained gray sandstone with a sericite binding material. It contains very thin dark streaks running parallel to each other, which, under the microscope, are seen to be enrichment zones of heavy minerals, mostly zircon and rutile. Sections of the mineral were cut and carefully polished by means of magnesia on a piece of flannel. On viewing the prepd. specimens under the microscope in transmitted light a few bright yellow particles of metallic appearance could be seen which readily became gray and rough on adding a small drop of Hg to the specimen, thus indicating Au. Pt could not be detected with certainty in this manner. 150 g. of the finely powdered rock was then treated with HF and  $\text{H}_2\text{SO}_4$  for several days on the water-bath. The residue, under the microscope, showed bluish white and yellow grains of Pt and Au, which were confirmed microchemically as K, Rb, and Tl chloroplatinates and as thallos chloroaurate, resp. J. S. C. I.



The ores of manganese. J. THORBAU. *Ann. Mines Belg.* 21, 2-43(1920); *Rev. géol.* 1, 355(1920).—A discussion of the obtaining of Mn ores for Belgian industries.

E. T. W.

Origin of Chilean nitrate. J. IGLESIAS TORO. *Caliche* 1, 77, 159(1919); 2, 198(1920).—It is assumed that the deposits are organic in origin, similar to the hypotheses of NOELLNER and of MÜNTZ and PLAGEMANN. The author attempts to det. during which geological periods the accumulations of marine growth and their decompn. to form the nitrate deposits occurred. Several analyses of the different types of deposits are given.

C. L. BURDICK

Kaolin in Belgium. E. ASSELBERGHS. *Ann. Mines Belg.* 21, 1059-67(1920); *Rev. géol.* 1, 292-3(1920).—Previously known deposits are discussed briefly and a new occurrence is described in detail. The kaolin from Ardenne is shown by a series of analyses to contain but 40% of impurities, which can be removed by levigation, yielding a product capable of competing with those of Devonshire and of Cornouaille; the latter in fact has to be sepd. from 75% of impurities.

E. T. W.

The limestone and phosphate resources of New Zealand. P. G. MORGAN, *et al.* *Bull. N. Zealand Geol. Survey* No. 22, 316 pp.(1919); *Rev. géol.* 1, 293-4(1920).—Analyses of many limestone deposits are quoted. The country has immense supplies of limestone, but transportation difficulties prevent its full utilization at present.

E. T. W.

The phosphorite of Terra d'Otranto. V. SIMONELLI. *L'Italia Agricola* Apr. 15, 1919, 9 pp.; *Rev. géol.* 1, 293(1920).—The phosphatic material occurs in calcareous tuff, as nodules which do not contain much more than 13% of  $P_2O_5$ . The possibilities of working it up are discussed.

E. T. W.

Some deposits of phosphates in Galicia, Podolia, and Palestine. V. SIMONELLI. *L'Italia Agricola* Oct. 15, 1919, 17 pp.; *Rev. géol.* 1, 354(1920).—Descriptions of the deposits are given.

E. T. W.

The supposed deposits of phosphate in Cirenaica. V. SIMONELLI. *L'Italia Agricola* Aug. 15, 1920, 10 pp.; *Rev. géol.* 1, 354(1920).—The calcareous clay reported to be phosphatic was found on analysis to contain but 0.45%  $P_2O_5$ .

E. T. W.

Extension of the Carboniferous into the littoral of Oran; the deposit of anthracite at Sidna Youcha, Nemours. M. DALLONI. *Compt. rend. somm. soc. géol. France*, June 21, 1920, 133-5; *Rev. géol.* 1, 296(1920).—The anthracite contains 70% of fixed C, 15-20% ash and 9% volatile matter. Its calorific value exceeds 7000 cal.

E. T. W.

Some Cretaceous lignites at Portabrubio, Teruel. M. FAURA Y SANS. *Bol. Soc. Españ. Hist. Nat.* 20, No. 7, 68 pp.(1920); *Rev. géol.* 1, 482-3(1920).—The lignite has sp. gr. 1.46, cal. value 3750 to 6470, ash 13.6 and S 1.64 to 5.72%.

E. T. W.

The story of petroleum. Pictures from the past history of our planet. ERNST BLUMER. *Neujahrsbl. naturf. Ges. Zurich* 1920, 1-27; *Rev. géol.* 1, 356(1920).—A popular account of B's. views on the origin of petroleum (C. A. 13, 3122-3).

E. T. W.

Origin of the Argentine petroleum deposits. GUIDO BONARELLI. *Anales soc. quim. Argentina* 7, 412 7(1919).—Because of the fossil remains found in the oil it is thought to be of animal origin. In some localities where volcanic action has occurred the oil is thick and heavy and contains much asphalt and aromatic hydrocarbons; this shows that cracking has taken place.

L. E. GILSON

Diffusion in silicate melts. N. L. BOWEN. *J. Geol.* 29, 295-317(1921).—In order to determine exptly. the rate of diffusion in fused rock-forming silicates the following procedure was employed: a layer of diopside was placed in the bottom of a crucible with a layer of plagioclase above it, diffusion was permitted at constant temp. (above the melting temp. of both layers) for a definite period, the charge was quenched and the compn. determined at various depths by measuring the  $n$  of the glass. From these expts. it would seem that the movement of large amts. of material through long distances



by diffusion cannot be credited when the rate at which the magma must cool is considered. On the other hand, diffusion through short distances is possible and such phenomena as the formation of reaction rims about foreign inclusions are to be attributed to diffusion, though for very wide rims (2 m.) a considerable period of time (100 yrs.) will be required.

W. F. HUNT

The physical chemistry of the crystallization and magmatic differentiation of igneous rocks. I. J. H. L. VOGT. *J. Geol.* 29, 318-50 (1921).—An article on crystn. and differentiation, pertaining to the application of the physical-chem. laws to the crystn. of magmas, also to the later crystn. of substances originally held in solid soln., and to the reactions which appear on the boundary between 2 minerals which are the result of the cooling of the rock after completed crystn. In the examn. of these laws 2 methods are employed (a) the synthetic, when precision detns. are possible, especially with reference to temp. and (b) analytic, which is based mainly upon a study of the structure of the rocks.

W. F. HUNT

Graphic representation of mineralogical-petrographic analyses, and petrogenetic considerations based thereon. J. MARCET-RIBA. *Bol. Soc. Españ. Hist. Nat.* 18, 496-504 (1918); *Rev. géol.* 1, 272 (1920).—Explanation of a new method of study.

E. T. W.

The basalt of Bühl near Cassel and its inclusions of magnetite, pyrrhotite, and native iron. W. IRMER. *Vorl. Ber. Senckenbergiana* 1, 71-6 (1919); *Z. Kryst.* 56, 110 (1921).—Dendritic to granular Ni-free Fe occurs in the rock.

E. T. W.

Results of the quantitative mineralogical analysis of the intrusive eruptive rocks of the calcareous-alkaline series. J. MARCET-RIBA. *Bol. Soc. Españ. Hist. Nat.* 19, 205-11 (1919); *Rev. géol.* 1, 334 (1920).—Detailed results and the conclusions drawn from them are given.

E. T. W.

Igneous geology of southeastern Idaho. GEORGE R. MANSFIELD. *Bull. Geol. Soc. Am.* 32, 249-66 (1921).—The igneous rocks described occur in the Cranes Flat, Henry, and Lanes Creek quadrangles and consist essentially of hornblende andesite porphyry, rhyolite and olivine basalt. The occurrence and description of each type are given, but no chem. data are included. It is thought that these rocks were formed from an original magma of intermediate compn. from which came first the hornblende andesite porphyry, and then by continued differentiation the series of rhyolites and basalts.

W. F. HUNT

The eruptions of historic time in the Canaries. I. FERNANDEZ-NAVARRO. *Mem. Soc. Españ. Hist. Nat.* 11 (No. 2a), 15 pp. (1919); *Rev. géol.* 1, 335 (1920).—This paper includes a number of analyses of the lavas.

E. T. W.

Outline of a systematic classification of figurative stones. A. ISSEL. *Mem. accad. Lincei* [5] 11, 41 pp. (1916); *Rev. géol.* 1, 426-7 (1920).—The objects here classified comprise concretionary, pisolites, stalactites, geodes, etc. In assigning them to classes their origin and chem. nature are considered.

E. T. W.

An organism producing magnesite. M. GIGNOUX. *Compt. rend. somm. soc. géol. France*, Feb. 4, 1918; *Rev. géol.* 1, 72 (1920).—As bearing on the problem of the origin of dolomite, it is pointed out that there is a very common protozoan, *Trichosphaerium*, the skeleton of which is formed entirely of  $MgCO_3$ .

E. T. W.

BETIM-PAES-LEME, ALBERTO: *Análise espectral aplicada a mineralogia*. Rio Janeiro, 1918. 138 pp. For review see *Rev. géol.* 1, 378 (1920).

Quantitative microscopic determinations of chalcophyrite, chalcocite, bornite and pyrite in a porphyry ore (HEAD) 7. Limestone deposits of New South Wales (CARNE, JONES) 20.



## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

**Flotation practice at Mount Lyell.** L. V. WATERHOUSE. *Proc. Australasian Inst. Mining Met.* No. 38; *Mining Sci. Press* 122, 87-93(1921).—The plant erected in 1916 treats ore from the Lyell Comstock and North Lyell mines. The former is a decomposed schistose ore containing chalcopyrite and pyrite, and assaying 2.6% Cu, 0.23 oz. Ag, 0.02 oz. Au, 48% SiO<sub>2</sub>, 11.5% Fe<sub>2</sub>O<sub>3</sub>, 1.4% BaSO<sub>4</sub> and 15.5% Al<sub>2</sub>O<sub>3</sub>. The North Lyell ore is more siliceous and contains bornite besides the pyrites. It carries 3.5% Cu with 66% SiO<sub>2</sub>. During 1919, 100 tons per day were treated with a recovery of 90.41% of the copper, 77.79% of the silver and 72.41% of the gold; the ratio of concs. was 4 to 1. A detailed account is given of the coarse crushing, fine crushing, tube milling, thickening, flotation and other departments, well supplemented with flow sheets and drawings of various new innovations.

A. H. HELLER

**Factors in the production of iron and steel on the Pacific Coast.** CLYDE E. WILLIAMS. Bureau of Mines. *Mining Sci. Press* 122, 94-6(1921).—Coking coals are scarce in the Northwest and the few that are available carry a high ash content. The presence of iron ore near the smelting locality is not as important as coke. There are extensive magnetite deposits in British Columbia which contain 50-60% iron, and the deposits of Southern California, west coast of Mexico and China can be drawn upon. There is an abundance of limestone and refractories both in the Puget Sound Region and in southern California. At the present time there is a market for only about 400 tons of pig iron daily, but this would be increased once the industry were established.

A. H. HELLER

**Chloride volatilization process.** THOMAS VARLEY AND C. C. STEVENSON. Bureau of Mines, *Repts. of Investigations* No. 2247, May, 1921, 9 pp.—Volatilization of metals as chlorides in metallurgical processes is still in the exptl. stage although studied for 20 yrs. A short history of development is given. It is especially suitable for oxidized ores of Cu, Pb, Ag, and Au for which gravity concn. and flotation are unsatisfactory and affords excellent means for separating Pb from Zn. The latter does not volatilize under oxidizing conditions. Expts. on sulfide ores are encouraging but these ores require preliminary roasting when more than 5% S is present. Chemical and microscopical data are necessary, the former providing for calcn. of chloride requirement, and the latter indicating required fineness of crushing. The reactions are probably reversible; chloride is formed at low temp. but not volatilized immediately. High temp. probably decomposes part of the chloride without volatilization. Chloridizing reagents may be volatilized without reacting with the ore; so that the most effective method is to add the reagents to the hot ore. Addition of 4% of CaCl<sub>2</sub>·2H<sub>2</sub>O increased volatilization of Ag from 74.3 to 90.3%. Baking and sintering may occur, the latter preventing chloridizing action. Ore flow, gas velocity, temp., and time are discussed briefly. Also in *Mining Sci. Press* 123, 153-62(1921).

G. R. J.

**The chloride volatilizing process.** HARM R. LAYNG. *Eng. Mining J.* 111, 1056-7 (1921); cf. C. A. 14, 1649.—L. considers Ca and Mg chlorides superior to NaCl as chloridizing and volatilizing agents. Special treatment as regards grinding, presence of H<sub>2</sub>O vapor, rate of heating, oxidizing conditions, rabbling, or method of adding the chloridizer are required for some ores. High extn. by the volatilizing process has been obtained on tailings from cyanidation of Tonopah ores. L. does not use the Cottrell system for recovery, but generally prefers an absorption system, and would use a bag-house when this method would not be suitable. The Cottrell method loses most of the Cl. Time required and fuel consumption in the volatilization process are much lower than has been stated.

A. BUTTS



**Chloridizing practice in Sweden.** NILS OSMAN. *Eng. Mining J.* 111, 1057 (1921).—Details are given regarding the compn. of the cement Cu obtained in the mechanical precipitator. Cf. C. A. 15, 1478. A. BUTTS

**Air conditions in the vicinity of smelters and the possibility of obtaining drier air cheaply.** J. BRONN. *Stahl u. Eisen* 41, 813 (1921).—From investigations at the Rombacher smelter at Koblenz it is found that the air at a height of 30 m. contains more than 20% less moisture than the air at a distance of 1.5 m. By having the inlets of the blowers or compressors at this elevation by means of suction towers the blast furnaces may be supplied with 35% drier air with very little expense. This decrease of the moisture content of the air with increasing distance from the earth's surface is not a general meteorological phenomenon but depends on the great amount of heat given out to the surroundings in the vicinity of smelters. It may be calcd. that for every gram of water contained in a cubic meter of air, 4 kg. are used in the blast furnace for every ton of pig iron smelted and that if the water increases 1 g. the coke used increases 6.5 kg., the amount of blast 1% and the amount of throat gases to heat the Cowper ovens 15 cu. m. By the use of the suction towers the moisture can be decreased many grams.

R. S. DEAN

**Occurrence of gold and other valuable minerals in the Transvaal.** L. ROSENTHAL. *Elektrochem. Z.* 27, 91-93 (1921).—This paper contains an enumeration of the mineral resources of the Transvaal including the extent and form of the gold-bearing ores found there. The most modern methods are used for working the ores. L. C. KRUEGER

**Notes on the influence of soluble silica and calcium salts on precipitation.** J. HAYWARD JOHNSON. *J. Chem. Met. Soc. S. Africa* 21, 191-3 (1921); cf. C. A. 15, 652, 1874.—White precipitate consists of approx. 70%  $Zn(OH)_2$  together with  $ZnCO_3$ ,  $CaCO_3$ ,  $Na_2ZnFe(CN)_6$  and a few other substances. It is thought that  $Zn(OH)_2$  is formed in the boxes as a result of very low cyanide strength and consequently low causticity,  $Zn(OH)_2$  being sol. in excess alkali and being thrown out of soln. as neutrality is approached.  $CaCO_3$ , which is an important factor, is formed partly by action of atmospheric  $CO_2$  but mostly from  $CaSO_4$  and  $Na_2CO_3$ , the latter resulting from decompn. of  $NaCN$ .  $Na_2ZnFe(CN)_6$  is practically all removed in the treatment tanks. Silica is always found in Au slime and other Zn box products and is generally attributed to imperfect classification, broken matting and drift sand carried by the wind. It is thought that all three causes contribute at times to the silicious content of Zn boxes. Another factor in bad pptn. is  $PbSO_4$  formed by the action of dil.  $H_2SO_4$  on some Pb compds.

H. C. PARISH

**Gases in aluminium furnaces and their analysis.** ROBT. J. ANDERSON AND J. H. CAPPS. *Chem. Met. Eng.* 24, 1019-21 (1921).— $CO_2$ ,  $CO$ ,  $(CN)_2$ ,  $H_2$ ,  $CH_4$ ,  $N$ ,  $O$ ,  $SO_2$ ,  $H_2O$  and unsatd. hydrocarbons are all common constituents of melting-furnace atmospheres. The proportions depend upon (1) kind and quality of fuel used; (2) type and design of the furnace; (3) operating conditions. A portable sampling app. is illustrated and described and the sampling procedure is given.  $CO_2$  is detd. by absorption in  $KOH$ ,  $O$  by potassium pyrogallate and unsatd. hydrocarbons by fuming  $H_2SO_4$ . The  $CuO$  combustion method is used for  $H$  and  $CO$  and the satd. hydrocarbons are detd. by slow combustion.  $(CN)_2$  is detd. by absorption in 2%  $NaHCO_3$  soln. and titration with  $I$ .

H. C. PARISH

**Losses in aluminium and aluminium alloy melting.** ROBERT J. ANDERSON. *Brass World* 17, 154-6 (1921).—Serious financial losses are incurred in melting non-ferrous metals, especially Al and its light alloys, because of the relatively high prices of these metals. Factors tending to a minimum of dross are now very worthy of attention because of the growing importance of the Al industry. The 3 essential requirements, low melting losses, rapid melting, and low melting costs, should each be considered.



At present the greatest variety of melting furnaces exists, though elec. furnaces are developing rapidly. Selection of the proper furnace is governed by particular plant conditions; there is no "best" furnace. Further difficulty results from the lack of available data regarding each type. The Bureau of Standards puts the Al losses at 2.5% and 5%, resp., for primary and secondary metal, or about 9,000,000 lb. per yr. (1918). The fuel efficiency is hardly above 5%. Thus probably \$2,000,000 could be saved yearly on the basis of 50% improvement.

F. H. HORCHAKISS

**Small-ball hardness testing machine.** ANON. *Engineering* 111, 612(1921).—A machine is described for testing the hardness of thin-walled tubes without internal support. It is possible to test objects only 0.01 in. thick. Thin material that would be disfigured by a large impression, such as cutlery blades, can be safely tested, the impression being so small that it is practically imperceptible to the eye without magnification.

V. O. HOMERBERG

**Brinell testing machine for large forgings.** ANON. *Engineering* 111, 680(1921).—A description is given of a machine of substantial construction that will accommodate work of considerable dimensions.

V. O. HOMERBERG

**Shock tests with notched bars.** LEGRAND. *Rev. metall.* 18, 225-8(1921).—L. disagrees with the selection of the Charpy shock test piece (see following abstract) by the Committee on Standardization because of superiority for metals of high resiliency. This opinion is a result of 18 tests on ordinary C and 2% Ni steels using both the Mesnager and standard test bars. The Mesnager bar gives 15-35% higher values for the same heat treatments; there is little difference in the angle of rupture. Additional tests should be made definitely to det. superiority.

W. A. MUDGE

**Shock tests with new types of test specimens by the Committee on Standardization.** LEON GUILLET. *Rev. metall.* 18, 221-4(1921).—As a result of several tests using 2% Ni, Mn-Si, Ni-Cr, and case-hardened ordinary C steels in the form of new designs submitted by Mesnager and Charpy, the Charpy piece was adopted because of superiority for metals of high resiliency. Its dimensions are 10 x 10 x 50 mm., with a round notch 5 mm. deep, 2 mm. wide at the top, and 1 mm. wide at the bottom. The Mesnager piece had the same dimensions, but its notch was only 2 mm. deep.

W. A. MUDGE

**Prism-hardness (of metals, etc.).** B. P. HATCH. *J. Inst. Mech. Eng.* 1920, 891-913. —Test pieces, preferably square prisms, of the same materials are used to indent one another, when placed cross-wise, and consistent hardness values are obtained by dividing the applied loads by the square of any characteristic linear dimension of the depression produced; measurement of the width gives the greater accuracy, but the depth is more easily measured. In the tests carried out the prism hardness,  $P. H.$ , was calculated from the formula  $P. H. = P/x^2$ , where  $P$  is the load and  $x$  the width of the indentation from corner to corner along the cutting edge. Among the metals and alloys tested were Cu, annealed and hard drawn; naval brass; delta metals; pearlitic steels with 0.18 and 0.43% C, forged, water quenched and tempered, and oil quenched; spring steel; austenitic Mn steel; and martensitic steel. Consistent results were obtained, the test being sensitive to slight differences of hardness even in the hardest metals. The scale of hardness given by this test is equally applicable to the hardest and softest metals.

J. S. C. I.

**Metallographic similarity in different states between steel, bronze, brass, and aluminium-bronze.** A. PORTEVIN. *Compt. rend.* 171, 350-3(1920).—P. notes the striking similarity between these alloys, each of which forms solid solns. when hot and gives eutectoids when cooled. Similarly to the successive austenite-martensite-transtite-pearlite series of steel, for bronze (Cu-Sn) there have been observed austenitic and martensitic states ( $\beta$  and striated  $\beta$  of Heycock and Neville). The eutectoid is generally



granular ( $\delta$  complex of Heycock and Neville), but the laminar and granular forms are sometimes coexistent. For Al bronze the austenitic form is rarely observed except in special alloys by quenching from the liquid state. The martensitic form has been described by several authors and the troostitic by Robin, who notes the analogy to steel. The two forms of the eutectoid also occur. For brass the austenitic form corresponds to that obtained on quenching very small ingots in water ( $\beta$  brass). The needle-like martensitic form may be observed in relief on polishing or also by etching. When brass is slowly cooled, as is ordinarily the case, the troostitic form is obtained, not resolved by the microscope. By very slow cooling (75 hours from m. p. to 300°) the eutectoid is obtained.

S. L. CHISHOLM

**Constitution of the alloys of aluminium, copper and zinc containing high percentages of zinc.** JOHN L. HAUGHTON AND KATHLEEN E. BINGHAM. *Proc. Roy. Soc. London* 99A, 47-69 (1921).—A detailed discussion together with many diagrams and a number of photomicrographs is given of the ternary system of Al, Cu and Zn.

V. O. HOMERBERG

**Recent research on special brasses.** L. GUILLET. *Compt. rend.* 171, 172-8 (1920).—Brasses contg. up to 5% Co have been prepd. and their phys. and mechanical properties detd. Such alloys offer no advantages over brasses contg. Ni. Attempts were made to introduce Cr into brass in the form of Cr-Ni alloy but only a small part (0.3%) of the Cr was retained in the alloy. Brasses containing Ag and Au to the extent of 1.67 and 1.07%, resp., were also prepd., the former metal has less effect upon the structure of the alloy than the latter.

S. L. CHISHOLM

**The effect of lead on zinc-bronze castings.** J. CZOCHRALESKI. *Z. Metallkunde* 13, 171-6 (1921).—A study was made of the mechanical properties of an alloy of Cu 88%, Sn 9%, Zn 5% to which amounts of lead varying from 0.2 to 6% were added. Metallographic examn. of the specimens also was made. C. concludes that: (1) lead up to 6% has no harmful effect on the physical properties; (2) lead makes the material much more readily worked and saves machining costs as well as improves the product; (3) the casting properties are much improved as the alloy not only melts at a lower temp. but is more fluid.

R. S. WILLIAMS

**Experiments with cast zinc alloys.** E. H. SCHULZ. *Z. Metallkunde* 13, 177-8 (1921).—Substitutes for various common metals and alloys were studied by the German metallurgists during the war. S. discusses some expts. with cast Zn alloys, giving in tabular form their physical properties and describing the methods of prepn. R. S. W.

**Bearing metals.** BRUNO SIMMERSBACH. *Chem. Ztg.* 45, 216-9 (1921).—A review of work on red brass (Cu-Sn) and white metal (Pb-Sb) bearing metals, describing the relation of composition, methods of manufacture, effect of impurities, and heat treatment to physical properties, and general uses. Most of the data are taken from the work of Heyn and Bauer, (*C. A.* 5, 3036; 6, 70).

W. A. M.

**The influence of additions on the anomaly of dilatation of iron-nickel alloys; application to the iron-nickel-chromium alloys.** P. CHEVENARD. *Compt. rend.* 172, 594-6 (1921).—By anomaly of dilatation is meant the progressive and reversible thermal transformation from one stable phase to another at a different temp., both being entirely miscible but different in density. This transformation for Fe-Ni alloys begins at very low temps., reaches a max. at Curie's point, and does not progress appreciably beyond this. Exptl. values between -183° and 900° are plotted as a function of coeff. of expansion and temp. From this curve and a normal curve (the derivation of which is not given in this paper) a differential curve is obtained, which, when extrapolated to abs. zero, gives total anomaly of dilatation,  $A_0$ . Values of  $A_0$  for different Fe-Ni alloys, containing 0.3-0.7% Mn, are plotted against compn., and a curve is obtained which rises from 25% Ni to a sharp max. at about 35% Ni, then falls rapidly and at 58% Ni crosses



the normal curve; between this point and 99% Ni the sign of  $A_0$  changes three times.  $A_0$  at the max. is  $6.1 \times 10^{-3}$ . Curves for alloys contg. 5, 10, and 15% of Cr are similar; the maxima are  $4.2 \times 10^{-3}$ ,  $2.6 \times 10^{-3}$ , and  $1.5 \times 10^{-3}$  resp. All four maxima correspond to  $\text{Fe}_3\text{Ni}$ . To explain this considerable decrease caused by Cr, the existence of  $\text{Ni}_3\text{Cr}$  is assumed since a projection of the max.  $A_0$  points on the ternary diagram crosses the Ni-Cr line at a point corresponding to 40% Ni.

W. A. MUDGE

**Cause of instability of nickel steel—its elimination.** CH. ED. GUILLAUME. *Compt. rend.* 171, 1039-41 (1920).—The instability of Ni-Fe alloys is shown to be due to the presence of small ams. of C as cementite. The addition of metals such as Cr, W, and V, with a higher affinity for C than Fe, greatly increases the stability. In accordance with the mass-action principle a considerable excess is required in order to obtain a product comparing favorably with an invar free from C.

S. L. CHISHOLM

**Expansion of nickel steel.** C. E. GUILLAUME. *Compt. rend.* 170, 1554-7 (1920).—The coeffs. for Mn and C in invar metal (35.6% Ni) have been detd., that of the former being  $0.12 \times 10^{-6}$  and of the latter  $0.5 \times 10^{-6}$  for each 0.1% of that constituent. The coeff. for pure Fe-Ni is  $0.2 \times 10^{-6}$ .

S. L. CHISHOLM

**Molybdenum steels.** JOHN A. MATHEWS. *Trans. Am. Inst. Mining Met. Eng.* 1921, No. 1059, 5 pp.—Mo steels, first made 25 years ago, were found unsatisfactory and inferior to V steels and so were abandoned. Owing to the supply of Mo in U. S. expts. were later continued and Mo steels are now used in airplane, automobile and general engineering trades. The principal difficulties with these steels are a tendency for Mo to volatilize at the high temp. necessary to work the metal and a lack of uniformity after prolonged or excessive heating. They can be worked in the mill over a considerable range of temp. Mo seems to exert most influence on reduction in area and, particularly with Cr, seems to confer the property of deep hardening. Mo steels require a higher drawing temp. for Mo tends to keep the C in metastable form. Below 1% Mo, there is no trouble from volatilization.

F. W. COHN

**Stainless steel, composition and properties.** ELWOOD HAYNES. *Iron Age* 107, 1467-9 (1921); *Blast Furnace and Steel Plant* 9, 518-9 (1921); cf. C. I. 14, 1803. Stainless steel must contain Cr and C in addition to Fe and may contain other elements. At least 8% Cr must be present to make the alloy inactive to atm. conditions, but, most products now contain 12-20%. Such steels resist atm. conditions better than Sn, Ni, Pb, Co, Cu, Ag, and many alloys. The C content should be 0.30-0.80%. Electric or crucible furnaces are used and hardness is controlled by rate of cooling. Hammering causes no scaling and drop forging is practicable. The steel can be immersed in salt water, boiled in  $\text{HNO}_3$ , dipped in  $\text{NH}_4\text{Cl}$ , vinegar, salt and vinegar, and citric acid without change. A steel with 40% Cr and a little Mo can be boiled in salt and citric acid. It can be heated to 800-1000° for an indefinite time without scaling. Sufficient annealing will cause a 15% Cr steel to be workable in a lathe and heating and cooling in air cause the material to become almost file hard. Elastic limit 115,000 lb. per sq. in.; tensile strength 200,000 lb. per sq. in.; elongation 2.5%; scleroscope hardness 80. The freshly prepd. product must be reheated and soaked before complete cooling, to prevent cracking and alloy chipping. This material is applicable for cutlery, cooking utensils, tools, and gas engine valves.

G. R. J.

**Prevention of hardening cracks and the effect of controlling recalcrescence in a tungsten tool steel.** SHIPLEY N. BRAYSHAW. *J. Iron and Steel Inst.* 1921 (advance copy) No. 1, 86 pp.—The paper describes an investigation carried out on a tool steel containing 1.1 C and 0.8 to 0.9% W. The changes that occur during the baths in heating and cooling were investigated by means of a large number of bars which, after soaking for various periods of time at temps. near the critical points, were quenched in  $\text{H}_2\text{O}$ . The condition of the steel after quenching showed the progress of the change; and some



of the results suggest that, both in heating and in cooling, the changes, Ac 1.23 and Ar 3.21, take place in stages which may be sepd. one from another if sufficient time be allowed for the process. A second series of bars, similarly heat-treated, was cooled in sand instead of being H<sub>2</sub>O-quenched. All these sand-cooled bars were finally hardened by 1 standard process. These bars lengthened or shortened on hardening, in response to the max. temp. of the previous annealing, and to the progress that had been made in the slow recalescence during that annealing. The behavior of the hardened bars under bending stress was also found to have been detd. by the heat treatment prior to the hardening. Light is thrown upon the subject by a comparison between those H<sub>2</sub>O-quenched bars referred to above, and these bars that were sand-cooled from the heat treatment and then hardened. The tendency of the steel to crack in hardening was correlated with the various results from the bars by means of a series of milling cutters purposely made of a design extremely difficult to harden. The milling cutters were machined out of blanks that had been heat-treated along with the bars. After the machining, the cutters all underwent the same standard hardening without any intervening process. The resulting cracks were found to occur in reasonable sequence with the treatment and with the results from the bars. When sufficient time was allowed for the heat treatment, within a certain range of temp., the steel reached a condition in which the liability to crack in hardening was greatly reduced. There was found to be a remarkable uniformity in the modulus of elasticity of the hardened bars, which differed greatly in other respects. Cutters that broke badly in hardening were generally made from blanks in which the ratio of the Brinell figure to the Shore figure was comparatively high. Progressive changes in length on successive days after hardening are referred to. A suggestion is made for a standard hardening test. V. O. H.

**Drill steel from hollow ingots.** P. A. E. ARMSTRONG. *Chem. Met. Eng.* 24, 960-4 (1921).—New practice at the Ludlum Steel Co. is to insert a high-grade, low-C mild-steel tube, suitably cleaned by sand blast, into an ingot mold and cast hot metal around the tube. The tube is filled with some air-excluding material, such as a high grade sand, to prevent oxidation and scaling of the inside. The ingots are then rolled in the usual way down to the finished bar, which is cut to proper size and the sand then extracted. A. claims that this method is superior to the Swedish method of rolling pierced billets because no carburization of the center results. The steel tube in the center increases the diameter of the center hole on freezing and therefore tends to overcome shrinkage cracks and strains. There is a greater freedom from external and internal straining due to a more uniform cooling rate, and an inherent smaller crystal size; less liability of the steel to crack in the inside of the hole during forging or hardening because of a pronounced toughening effect arising from the mild-steel wall of the hole, which limits the intense hardening on quenching. There is no weakness of the wall of the hole because of an absence of harmful segregations. The method gives greater safety for uses when overheating must be contemplated since the ultimate grain growth will be less than in an ingot of similar size cast solid, because the crystals were originally smaller. Less chipping and grinding are required if proper casting temps. and conditions are observed.

W. A. MUDGE

**Relation of heat-treatment to cold-work in hypo-eutectoid and eutectoid steels.** A. T. ADAM. *Iron Steel Inst. (London), Carnegie Schol. Mem.* 1920, 65-127.—The expts. described were undertaken to study the processes used in wire-drawing practice, and were confined to this form of cold-work. Most of the expts. were carried out on two steels, one a basic open-hearth steel contg. C 0.44%, Si 0.06%, Mn 0.82%, S 0.036%, P 0.031%; the other an acid open-hearth Swedish steel contg. C 0.85%, Si 0.12%, Mn 0.30%, S 0.022%, and P 0.02%. To det. the effect of heat treatment in prepn. for cold-work the steel, in the form of 4 or 5 S. W. G. rod, was heated to 850°, 950°, or 1050°



and then cooled in air or quenched in lead at 500° or in oil and reheated to 600°. In the case of the basic open-hearth steel the capacity to withstand cold-work increased with the temp. with air-cooling. With Pb quenching lower temps. gave better results, but the differences due to temp. were so slight that it may be concluded that the safe working range of temp. in the "patenting" process is extremely wide. Expts. with other steels confirmed this, and indicated that one of the objects of "patenting" is to enlarge the grain rather than to refine it. A good wire is produced from what would normally be an over-heated steel. With steel of eutectoid compn., i. e., of about the compn. of the above Swedish steel, there is no advantage in "patenting" beyond 950°. The improvement obtained by quenching in Pb is more marked in these steels than in medium steel. Heating below the crit. range does not remove the effects of previous cold-work and cannot replace "patenting." Expts. on the effect of heat treatment after cold-work showed that hot galvanizing has a bad effect on the physical properties of the wire, and the higher the tenacity of the wire, the more serious is the effect. Time is an important factor, especially as regards its influence on the max. load. The temp. of the galvanizing bath should be as low as possible and the immersion should be as short as possible, consistent with the production of a satisfactory coating of Zn. The work on the microstructure showed that a fine-grained structure is unsuitable for wire-drawing. The most suitable structure is one in which the grains are large enough to elongate into fibers and which consists throughout of granular or cellular sorbite. A structure of laminated pearlite, as in annealed eutectoid steels, is unsuitable. The structural effects of heat treatment after cold-work are scarcely visible until recrystn. commences. When this occurs the ferrite forms new grain boundaries and the cementite collects in the form of nodules which tend to coalesce. J. S. C. I.

**Inversely hard castings.** P. BARDENHEUER. *Stahl u. Eisen* 41, 570-75, 719-23 (1921).—Hard castings are sometimes produced in which the center of the castings and the thick sections are harder than the surface and the thin sections; since this is the reverse of the usual conditions these castings have been called inversely hard castings. The following conclusions as to their cause are drawn: (1) The entire casting crystallizes as a white iron owing to supercooling; the marginal zone then becomes gray through the sepn. of temper carbon. This explanation is confirmed by the artificial prepn. of inversely hard castings. (2) The reasons for super-cooling are usually too high S and too low a pouring temp. R. S. DEAN

**New methods for hardening iron and steel.** W. HACKER. *Elektrochem. Z.* 27, II, 49, 57, 68(1921).—A review, with brief description of the suggested improvements for hardening steel as brought out in the literature and patents since the beginning of the war. W. E. RUDER

**Heat treatment of steel.** G. W. YALE. *Engineering* 110, 273(1920); *Science Abstracts* 24B, 17.—Y. advocates elec. furnaces for the heat treatment of steel. In furnaces or lead baths of great heat capacity, the introduction of the material causes little cooling down and small parts heat up more quickly than large parts, frequently with disastrous results. Steel expands when heated, both below and above the transformation points, but at the actual transformation contracts; hence if different portions of a mass of steel under treatment pass the transformation point at different times, distortions are likely to occur, and there may be cracking and failure. If a similar piece of steel be heated in an elec. furnace of small heat capacity, the furnace is chilled on the introduction of the metal, and the temp. of the whole can then be raised slowly, in which case both the light and heavy portions pass through the transformation range at the same time. H. G. Z

**Solubility of graphite in molten iron.** RUDOLF RUER AND JULIUS BREN. *anorg. allgem. Chem.* 113, 98-112(1920).—The soly. of graphite in Swedish Fe has been



detd. by heating the Fe with graphite until satd., and then pouring the molten metal into a metal tube so that it was cooled too rapidly for the dissolved graphite to sep. The metal was then dissolved in  $\text{HNO}_3$  (d. 1.18) and the graphite detd. in the usual way. Estns. were made at temps. from 1152° to 2500°. Above 2500° approx. detns. show that the soly. continues to increase up to 2700°. The soly. curve of graphite in molten Fe is linear from 1152° to 1700°, when it bends slightly at first and with increasing temps. more markedly away from the concn. axis. Examn. of sections of the chilled metal showed graphite, cementite, and austenite, but no further cryst. substance. The concn. of the graphite eutectic which lies at 1152° is 4.25% C, that of the cementite eutectic which lies at 1145° is 4.30% C. The thick liquid which is formed when graphite and molten Fe are in contact, with rising temp., is due to the dissolved C, and the only action of the increased temp. is that it increases the soly. of the C in Fe. J. C. S.

**The rate of diffusion of carbon in iron.** I. RUNGE. *Z. anorg. allgem. Chem.* 115, 293–311 (1921).—The velocity of diffusion of C in electrolytic Fe was detd. by measuring the change in resistance of a helix of Fe wire heated at 600°, 700°, 800°, and 900° in an atm. of various gases containing C. The following gases were used: illuminating gas, a mixt. of illuminating gas with H, and mixts. of H or N with the vapors of hexane, benzene, toluene, MeOH and petr. ether. The resistance of the wire increased with increasing C content, gradually approaching a const. max. which represented the resistance of iron satd. with C at the temp. of the expt. The resistance of the wire did not change in any expt. conducted at 600° or 700°. At 800° mixts. of petr. ether with H and of hexane with N gave slow rates of increase in resistance, whereas at the same temp. a mixt. of hexane with H gave a rapid rate. At 900° a mixt. of illuminating gas with H and of MeOH with H had no effect on the resistance of the wire; illuminating gas, a mixt. of toluene with H, and another of toluene with N gave slow rates of resistance increase; and a mixt. of benzene with N, one of petr. ether with H and another of hexane with N gave rapid rates of resistance increase. From the standard equation for expressing the rate of diffusion R. deduces an equation from which the carbon content after any time interval or at any section of a specimen can be computed. Two cases are considered: first, the rate of soln. is faster than the rate of diffusion; second, the rate of soln. is slower than the rate of diffusion. By substituting exptl. values in these equations the coeff. of diffusion for C in Fe was detd. This coeff. represents the amt. of C that will diffuse in unit time through unit surface under a concn. gradient of unity. From these equations 2 others were deduced for the 2 cases described above, which represent the resistance of an iron wire, exposed to carbonizing gases, at any time interval after soln. of the C begins or the resistance for any C content. Curves plotted with values obtained from these equations agreed closely with observed values. These expts. did not show whether C dissolved in Fe as solid C or as a gaseous hydrocarbon or whether it dissolved in both forms. The increase in the rate of soln. observed in those expts. in which H was present indicates possibly that the rate of soln. is more rapid if the C is present as a hydrocarbon. It is concluded that: (1) The diffusion of dissolved C in iron follows the standard equation for the expression of the rate of diffusion. The coeff. of diffusion at 930° is  $(2 \pm 0.2)10^{-7}$  cm.<sup>2</sup>/sec. At 930° approx. 0.6 mg. of C passes through each cm.<sup>2</sup> of exterior surface in the first 3 min. of exposure to a rapidly carbonizing gas. (2) The change in resistance caused by 1% C content is, at about 920° 5.7%, at 830° 7.0% of the resistance in the hot condition; at 18° about 40% of the resistance in the cold condition. (3) The velocity with which gases and vapors containing C can yield C capable of diffusing varies with the nature of the gas mixt. and with the temp. (4) That pure  $\beta$ -iron as such cannot hold C in solution does not prevent carburization at those temps. at which the iron originally is in the  $\beta$  form. F. P. FLAGG



**Magnetic analysis as a critical test for the quality of steel and its products.** C. W. BURROWS AND F. P. FAHY. *Am. Soc. Testing Materials* 1919, p. 46; *Rev. mét. all.* 17E, 315-20(1920); *Science Abstracts* 23B, 571.—The authors have used the ballistic ring method, the Fahy permeameter and a special yoke app. for investigating the magnetic properties of steels from the point of view of their suitability for certain com. purposes (blades for cutlery, steel rails, etc.). *B-H* curves are given in the paper showing the effect of quenching in oil and water when the sample has been heated to various temps. up to and beyond the crit. temp. An increase in the rapidity of quenching starting from a temp. above the crit. temp. has approx. the same effect upon the magnetic and mechanical properties as an increase in the C content. The coercivity is considered the best criterion for testing the mechanical hardness. It is also shown how the leakage along a steel rail magnetized in the yoke can be used as a test for detecting the presence of blow-holes and fractures.

**Grinding cracks.** LÉON GUILLET, JEAN GALIBOURGH AND PIERRE BEURET. *Rev. metall.* 18, 213-20(1921).—Cracks produced on grinding case-hardened axles and gears are due to uneven local heating of the steel by the emery wheel and not to the method of hardening, or segregation of cementite. (Cf. C. A. 13, 1701). The heating also causes an appreciable softening due to annealing. By rapid turning of the pieces during grinding, and cooling with a stream of water the cracking can be entirely eliminated. Best results are obtained by rotating the steel in the same direction as the wheel, and as rapidly as possible. The study will be continued. W. A. MURK.

**Non-rusting chrome-nickel steels.** B. STRAUSS. *Naturwissenschaften* 8, 812-4 (1920).—Chrome steels show great resistance to corrosion, but without Ni have not the requisite mechanical properties. There are two groups of chrome-Ni steels, showing high resistance to corrosion but differing essentially in physical and chem. properties and in structure. To the first group belong steels having a martensitic structure and contg. 10-15% Cr with 1-3% Ni. These are self-hardening. By heating slightly above the transition temp., 680-750°, and cooling slowly or quickly, they assume a troostosorbite structure and become workable. The second group of chrome-Ni steels, with 20-23% Cr and 6-9% Ni, have a polyhedral structure (austenite) and require a different heat treatment, consisting in heating to 1100-1200° and cooling quickly. Unlike those of the first group, these steels are non-magnetic. In both groups the C content is 0.1-0.3%. Between the two groups lie steels with intermediate structure and unfavorable mechanical properties. The oxidation potential of these non-rusting steels is between that of Cu and that of Ag. J. S. C. I.

**The gap between theory and practice in the production of corrosion-resisting iron and steel.** WM. D. RICHARDSON. *Trans. Am. Electrochem. Soc.* 39, preprint(1921).—A general review of the corrosion problem. The subject matter is treated under the following headings: general considerations; empirical results; lack of data; the electrolytic theory; the influence of rust; corrosion tests; Cu-bearing Fe; Si-containing cast Fe; duriron; Ni steels; Ni-Cr steels; Ni-Cu steels; Cr steel; Ni-Cr-Co alloys. Since O is the dominating influence in "ordinary" corrosion, corrosion can be prevented by maintaining a passive surface or by means of adherent rust or adherent magnetic oxide. Or corrosion can be prevented by avoiding the O influence: (a) by changing the composition of the metal so that the O influence is of no effect, (b) by means of protective coatings, paint, etc. C. G. F.

**The corrosion of old iron.** E. A. RICHARDSON AND L. T. RICHARDSON. *Trans. Am. Electrochem. Soc.* 39 (preprint); *Chem. Met. Eng.* 24, 842(1921).—Analyses are tabulated of 15 specimens of Fe and steel which have been subjected to atm. corrosion, in some cases for as much as 25 years. Five contg. over 0.10% Cu were in good condition, while of 10 contg. less than 0.10% Cu, 5 were in fair to good condition and the



remainder in poor condition. Comparative tests, over a period of two years, of old and of recently made Fe of about same Cu content show the former has no greater rust-resisting characteristics than the latter.

W. H. BOYNTON

**The action of inks on metallic iron.** I. O. BAUER AND WERNER MECKLENBURG.

*Mitt. Materialprüfungsamt* 37, 63-84 (1919).—Two kinds of commercial steel pens were subjected to the action of an iron-gallate trade ink for 3 days at room temp. One lot of pens lost 32.6-90.6 mg. in weight and the other lost 43.2-110.2 mg. Qual. tests on other inks indicated a reversal of the amount of corrosion. To supplement these results and to det. the cause of corrosion, B. and M. conducted the following expts. in duplicate. Small pieces of ingot iron (99.17% Fe), 20 x 20 x 0.7 mm., were immersed in 13 different iron gallate inks ("E" inks), 7 different tannate or oxalate trade inks ("U" inks), 15 different aniline dye inks, and dil. solns. of HCl and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> containing as much iron (6.05 g./l., as FeCl<sub>3</sub>, FeCl<sub>2</sub>, or FeSO<sub>4</sub>) and acid as found in the other inks used. The time varied from one to thirty days. The following conclusions were noted: (1) Ingot iron is 50% less corroded than steel pens; (2) amt. of corrosion increases with acidity; (3) corrosion can be calcd. from  $V = at^b$ , where  $V$  = loss in wt. in mg.,  $t$  = time in days, and  $a$  and  $b$  are consts., for periods not exceeding 20 days; (4) oxalate inks produce less corrosion than the others owing to the pptn. of FeC<sub>2</sub>O<sub>4</sub> aq. on the iron or steel pen, since this forms a "protective coating"; (5) corrosion by aniline dye inks depends largely upon the kind and nature of the dye used in their manuf.—some dyes increase and others decrease corrosion; (6) iron inks containing ferric salts are especially bad since they are reduced to ferrous salts according to the equation,  $2\text{Fe}^{+++} + \text{H}_2 \rightleftharpoons 2\text{Fe}^{++} + 2\text{H}^+$ , the acidity and consequently the corrosive property of the ink being thereby increased. Improvements should be made in both the pen and ink industries to produce non-corrosive pens and low-acid inks. The article gives detailed exptl. results and analyses and must be consulted for specific cases. II. *Ibid.* 322-34.—In addition to the gallate and tannate inks, B. and W. employed 3 different logwood inks, and 2 each of red, green, blue and violet writing inks, and compared these with the corrosion produced by distd. water, a 1% NaCl soln., and 0.05 N, 0.1 N, and 0.2 N solns. of HCl and H<sub>2</sub>SO<sub>4</sub>. The time period was reduced to one to four days, and the temp. controlled throughout, at 18°, by means of a thermostat. The general conclusions are similar to those previously reported.

W. A. MUDGE

**The cause of corrosion of steam boilers.** G. PARIS. *Chaleur et industrie* May, 1920; *Rev. gén. élec.* 9, 182-5 (1921); *Science Abstracts* 24B, 108.—A summary of investigations in the lab. of Paul Kestner in Paris on boiler corrosion. P. discusses the subject from both the theoretical and practical standpoints. The dissolved gases and not the salts of the feed-water are the real cause of internal boiler-plate corrosion. When the dissolved O and CO<sub>2</sub> are eliminated from the water before it enters the boiler, the internal corrosion of the boiler almost entirely ceases. The usual method of removing the dissolved O by preheating the feed-water was investigated, and found ineffective as a means of removing all traces of the gas; and the passage of the feed-water through a series of vessels contg. Fe turnings specially prepd. for the purpose of removing the O was requisite, in order to achieve the objects aimed at. The conclusions are that the complete removal of the O from the feed-water paralyzes the corrosive action of both CO<sub>2</sub> and dissolved salts, and that this removal of the dissolved O can be cheaply effected by the method described. Cf. Perdrietz (*Rev. gén. élec.* 9, 185-7 (1921)). H. G.

**Rusting of steam boilers.** G. BRUNN. *Z. angew. Chem.* 34, Aufsatzteil, 231-2 (1921).—The boiler tubes were fed with an untreated, brackish water from a peaty soil, mixed with an overflow from a nearby cesspool. In addition to Ca salts the water contained appreciable amts. of sol. nitrates and humic acid. The pptn. of CaCO<sub>3</sub> and elimination of CO<sub>2</sub> on heating left the water sufficiently acid to cause a reaction between



the nitrates and humic acid, resulting in the formation of a small amount of free  $\text{HNO}_3$ , which attacked the boiler tubes and walls,  $\text{HNO}_3$  and  $\text{NH}_3$  being formed. The decomposition products of humic acid or their Ca salts have a dark reddish brown color, and gave an exaggerated idea of an accelerated corrosion which was not found on actual inspection of the boiler walls.

W. A. MUDGE

**Unusual boiler tube corrosion by carbon dioxide.** BARZILLAI G. WORTH. *Trans. Am. Electrochem. Soc.* 39, preprint(1921); *Chem. Met. Eng.* 24, 843(1921).—A steam boiler corroded rapidly and resisted all attempts to protect it electrolytically. Finally the trouble was located as due to soluble Fe bicarbonate in the water used, which gave off large quantities of  $\text{CO}_2$  when heated in the boiler. The water was then treated by keeping it at the h. p. 8 hrs. in a preheater, where the  $\text{CO}_2$  was liberated and a sludge of  $\text{Fe}(\text{OH})_3$  pptd. The trouble then ceased.

J. W. R.

**Metal coatings for rust prevention. (Zinc.)** W. LANGE. *Z. Metallkunde* 13, 167-70(1921).—The four common methods of applying zinc coatings are discussed: electrodeposition, hot-dipping, sherardizing and the Schoop process. Corrosion expts. were tried with each method with different corroding agents. The effectiveness of the four methods is about the same when each is applied in the best way. The choice of type of coating depends on the nature of the article to be coated. For example, hardened and hard-drawn pieces should be electroplated, plates, pipe, etc., should be sherardized or hot-dipped and cast iron should be sprayed.

R. S. WILLIAMS

**Slip interference theory of the hardening of metals.** ZAY JEFFRIES and R. S. ARCHER. *Chem. Met. Eng.* 24, 1057-67(1921).—Hardness is resistance to permanent deformation. Metals fail under stresses much below their ultimate strength (as measured by the interatomic forces holding the atoms together) because they are built up of crystals. Since the atoms are arranged in crystals according to some definite spatial form planes of weakness are present in the crystals. Fractures start along these planes. If fracture takes place without the fragments formed adhering the fracture is said to be brittle and the plane of weakness is called a cleavage plane. If the fragments adhere and merely glide over one another the crystal is ductile and the plane of weakness is called a slip plane. Anything that hinders slip increases the hardness of the crystal. The crystals in a metal are surrounded by a sheath of amorphous metal which is stronger than the crystalline phase. Therefore, decreasing the size of the crystals will increase the hardness. Solid solns. are harder than any of their components, owing to the interference of the atoms of the solute with the form of the slip planes. The increased hardness of aged quenched duralumin specimens is caused by the pptn. within the crystal grain of the hard constituent  $\text{CuAl}_2$ . In this example the effect on hardness caused by varying the size of the dispersed hard particle can be explained as follows: The dispersion which produces maximum hardness is called the "critical dispersion." Dispersions finer than this are classified as "sub-critical"; those coarser as super-critical. In the sub-critical condition time has not been allowed for the atoms to fix themselves in the form of their typical crystalline arrangement. This is the state of the metal in the quenched condition, and any increased hardness in this condition is that which all solid solutions have. As time is allowed the atoms are given an opportunity to form the crystals of the hard constituent. As first formed, these are small and numerous. Soon enough are formed so that they obstruct motion along many slip planes. Thus increased hardness results. This is the condition of the metal in the critically dispersed state. The hard particles constantly increase in size, the smaller particles uniting, and as their size increases the number of slip planes obstructed decreases and, therefore, the hardness decreases. The "super-critical" condition is reached. Austenite is a solid soln. of carbon in gamma iron. "When the rate of cooling of austenite is sufficiently rapid to form martensite, the transformation of the gamma iron to alpha is substan-



tially complete whereas the formation of cementite is not complete." Martensite consists of submicroscopic ferrite crystals containing carbon in soln. The hardness of martensitic steels results from the extremely fine grain size of its ferrite and from the hardening effect of the carbon atoms dissolved in the ferrite. During the tempering of martensitic steels two changes occur; one decreases the hardness and other increases it. The softening results from the growth of the ferrite crystals and the hardening from the pptn. of cementite. As tempering progresses the cementite particles increase in size, reaching the dimensions described as super-critical, and thus decrease the hardness.

F. P. FLAGG

**Significance of recrystallization.** G. TAMMANN. *Z. anorg. allgem. Chem.* **113**, 163-78 (1920); cf. *C. A.* **13**, 3138.—The recrystn. of metals when worked cold is discussed. It is known that when metals are worked cold or at temps. much below the m. p. large crystals are produced at the expense of the smaller crystals. The older distn. hypothesis put forward to explain the process is considered and shown to be incapable of successfully explaining it. T. puts forward a new hypothesis to explain the process, and considers a number of facts in connection with recrystn. from the point of view of this hypothesis, and in all cases finds it satisfactory. The hypothesis is as follows: Two contiguous crystals can only be in equil. with one another when the crystallographic equil. lattice planes of both crystals lie together in the same plane at the surface of contact, that is, when the space lattices of both crystals of the contiguous crystals form a single lattice or when the plane of contact is a twinning plane. If one or the other of these conditions is not fulfilled, then when the temp. is raised sufficiently to allow of a certain amt. of change in the position of the atoms or mols. in the lattice, new lattices of mean orientation to the surface of contact will be formed, that is, a recrystn. will commence.

J. C. S.

**Liberation of gas from cold-worked metals during recrystallization.** G. TAMMANN. *Z. anorg. allgem. Chem.* **114**, 278-80 (1920).—On heating a drawn Cu wire in a vacuum, gas was evolved, the rate of evolution being greatest between 200° and 300°. At this temp., the alteration of structure of the cold-drawn wire is also most rapid. The evolved gas gave the spectra of CO and CO<sub>2</sub>. Electrolytic Fe showed in the first heating a max. rate of evolution of gas at 530-600°; in the second heating at 610-50°. The spectrum of the gas showed the lines of H and CO. A sublimate of Ph was obtained from the Fe. This is observed only when the metal has been cold-worked before heating in a vacuum.

J. C. S.

**Researches on the elastic properties and the plastic extension of metals.** W. E. DALBY. *Trans. Roy. Soc. London* **221A**, 117-38 (1920).—A continuation of previous work with reference to the load-extension and looped diagrams. (Cf. *C. A.* **7**, 3306; **9**, 49).

W. A. MUDGE

**The detection of parts of different "nobility" in a piece of metal.** S. KYROPOULOS. *Z. anorg. allgem. Chem.* **114**, 157-60 (1920).—Different parts of a piece of metal may exhibit different behavior in certain solns., on account of differences of elec. potential. Thus, when a clean nail is placed in an agar gel contg. K<sub>4</sub>Fe(CN)<sub>6</sub> and phenolphthalein, the metal at the point appears more "noble" than that at the head; in the neighborhood of the point a red color develops, on account of the formation of free OH<sup>-</sup> ions, while along the surface of the nail a blue color appears, owing to the production of Fe<sup>3+</sup> ions. The difference is due to the greater degree of working to which the metal towards the head of the nail has been subjected. If K<sub>4</sub>Fe(CN)<sub>6</sub> is substituted for ferricyanide in the soln., it may be used to detect similar local differences in pieces of Mn, Zn, Cd, Al, Ni, or Cu. If a clean Ag plate is scratched and immersed in an agar soln. contg. KI and phenolphthalein, the scratches show up as black lines on a bright ground, through the deposition, on the less "noble" worked parts, of AgI. With proper choice of in-



dicators, the method should be generally applicable to the detection of chem. and physical inhomogeneity in the surface of a metal. J. C. S.

**Occurrence of a foliated appearance on strips of sheet zinc.** E. H. SCHULZ AND R. MELAUN. *Forschungsarb. Geb. Ing. Sonderreihe M* [1], 23-7.—On bending and twisting several different kinds of sheet Zn it was noticed that the surface split up into small leaves, giving the material a foliated appearance. While this could be traced partly to segregation of the Pb in rolling, it otherwise did not appear to have any connection with the chem. compn. of the metal and was probably due to the method of rolling, the metal having been rolled out in fewer stages than usual, thus giving rise to temp. differences between the outer surfaces and the interior. This produced small longitudinal cracks along the edges of the rolled sheet and on the broken edges of a fracture, and on bending the metal caused the foliated appearance. No explanation, however, could be found for the fact that Rhenish and Belgian zincs behave worse under these conditions than Zn of similar compn. produced in Upper Silesia. J. S. C. I.

**Influence of the forging temperature on the tensile properties of forged zinc.** E. H. SCHULZ AND R. FIEDLER. *Forschungsarb. Geb. Ing. Sonderreihe M* [1], 27-29.—Tests made on Zn rods (contg. 1.3% Pb and a trace of Fe) forged down from 120 mm. to 50 mm. diam. at various temps. showed that the highest tensile strength and elongation were obtained when the forging temp. was 120°. As this temp. was increased the ultimate stress altered but little, but the elongation and resistance to impact of the resulting bar were considerably decreased, while the metal became coarser grained. Metal contg. more Fe must be worked at a higher temp. than pure Zn, and if worked just below 120° it gives a greater elongation. J. S. C. I.

**Behavior of zinc in the impact test.** E. H. SCHULZ AND R. FIEDLER. *Forschungsarb. Geb. Ing. Sonderreihe M* [1], 29-31.—Forged Zn with a tensile strength up to 20 kg. per sq. mm. and an elongation of 30% or more gave results in the impact test with a notched bar varying from 0.55 to 0.75 kg. m. per sq. cm., and this figure could not be improved upon by prep. the specimen by other methods, by further refining, or by alloying the Zn with other metals. The results obtained with bars with V-shaped notches decreased as the angle of the notch increased, and the broken bars showed a short granular fracture. Bars with a circular notch had a resistance several times as great as that of those with angular notches, and the fractured surface was very jagged. Tests at various temps. showed that the resistance of Zn to impact decreased with fall of temp. J. S. C. I.

**Development of a coarsely crystalline structure in forged zinc by heating.** E. H. SCHULZ AND O. ZELLER. *Forschungsarb. Geb. Ing. Sonderreihe M* [1], 32-8.—By heating forged Zn for  $\frac{1}{2}$  hr. at gradually rising temps. from 100° upwards and examing the fracture and microscopic structure of polished and etched surfaces, it was established that, at a definite temp., depending on the forging temp. of the sample, but at least 140°, a fairly sharply sepd. zone of larger grained metal developed round the outer edges of the test piece. As the temp. was raised this zone gradually increased in extent until at 200°, or higher, according to the original forging temp., complete recrystn. of the metal took place. As the grain of the metal became coarser the tensile strength, and especially the elongation, decreased, the latter very considerably after recrystn. had set in, but no change was noticed in the Brinell test. Heating Zn to 150-200° has a bad effect on the elongation. The tensile strength is not appreciably altered by heating for  $\frac{1}{2}$  hr. at 200°, but at 300° a considerable decrease in strength is produced. J. S. C. I.

**Effect of addition of copper and aluminium on mechanical properties of forged and rolled zinc.** E. H. SCHULZ AND R. MELAUN. *Forschungsarb. Geb. Ing. Sonderreihe M* [1], 38-42.—Addition of 2 1/2% Cu to forged Zn increases the tensile strength and



hardness of thick bars to an extent depending on the temp. of forging, but does not appreciably improve the ductility or the toughness. Similar results are obtained by the addition of Al up to 4.4%, but in this case the metal appears to be more brittle. Thick plates that have been rolled from 30 cm. down to 1 cm. have good tensile strength and ductility combined with a low hardness number if 2% of Cu has been alloyed with the metal. Addition of Al does not give such good results, it being necessary to add more than 4% Al to get the same effect as with 2% Cu, and even then, for the same tensile strength the elongation is less than that of the Cu alloy. According to the particular method of working forged Zn with 2% Cu, the elongation and contraction of area vary from 9 to 30%.

J. S. C. I.

**The purification and testing of aluminium.** FRANZ MYLIUS and WERNER MYLIUS. *Z. anorg. allgem. Chem.* 114, 27-64 (1920).—Expts. were made on the further purification of technical "pure" Al, which may contain Al 99.58, Fe 0.18, Si 0.22, C 0.02%. When such a metal crystallizes slowly, practically pure Al first crystallizes, the impurities crystg. last in the eutectic. Such Al can be granulated by stirring the metal during crystn., and by extg. the granules with dil. HCl most of the Fe can be removed. By repeating this process 3 times, a metal was prepd. contg. Al 99.9, Fe 0.02, Si 0.2, C 0.01%; the loss was 50%. Purification can also be effected by partly melting the metal and sepg. the less pure liquid portion from the purer Al crystals, but the process is tedious and the yield of pure metal is low. Expts. were made with the object of devising a test for detg. the probable behavior of technical Al when exposed to atm. influences. It was shown that Al of the highest obtainable purity is but slightly attacked by 20% HCl and by other corrosive agents.

J. C. S.

**Producing small non-ferrous castings.** RAYMOND H. SULLIVAN. *Metal Ind.* 19, 108-11 (1921).—Description of the method of producing small castings at the Yale and Towne Mfg. Co., Stamford, Conn.

R. S. D.

**Importance of the pyrometer in industry.** CLIFFORD W. NASH. *Ind. Australian Mining Standard* 64, 1171-3 (1921).—Consideration is given to the use of the pyrometer in obtaining cooling curves and its application in the hardening and tempering of steel and in the manuf. of malleable cast Fe.

V. O. HOMERBERG

**Electric arc welding.** M. LEBRUM. *Rev. metall.* 18, 201-12 (1921).—After reviewing Kjellberg's and LeChatelier's work L. gives results of torsion, alternating stress shock, and tensile tests on welded and riveted bolt rings in comparison with the original, mild carbon steel. Welded specimens, 6-14 mm. thick, have 63-96% of original strength and are generally 10% superior to riveted specimens. Welding reduces C, Si, and Mn, but does not alter S and P. The effects of dilatation are reduced to a minimum. The technic is simpler and easier than with the torch, and therefore manual labor is reduced. Analyses and photomicrographs are given, together with a brief discussion of successful applications of arc welding in the manuf. and repair of marine and locomotive boilers, locomotive hearths and other parts.

W. A. MUDGE

**Thermite welding and electric arc welding.** G. LANGE. *Elektrotechn. Z.* 42, 722-4 (1921).—An address. 4 illus.

C. G. F.

**Sulfur recovery from blast-furnace slag (DIEHL) 18.** Phenomena in the formation of space lattices composed of two different species of atoms, particularly in the formation of mixed crystals of silver and gold (TAMMANN) 2. Electromotive behavior of magnesium-mercury alloys (KREMANN, MÜLLER) 2. Electromotive behavior of aluminium-mercury alloys (KREMANN, MÜLLER) 2. Transformer tanks of copper-alloy steel (BINGAY) 4.

**Recovery of copper.** M. TSUGAKI, D. HAYASHI, Y. NISHIKAWA, AND KÔRÊKI



SYOKUSAN Co. Japan 36,590, June 15, 1920.  $\text{CuSO}_4$ , obtained by burning Cu contained in  $\text{FeS}$ , etc., is heated with an aq. soln. of  $\text{NaCl}$ ,  $\text{MgCl}_2$  or concd. sea-water, during which operation waste gas containing  $\text{SO}_2$ , air, and  $\text{H}_2\text{SO}_4$  produced in the burning process of pyrite etc. is blown into. The sulfate is changed to chloride, which is extd.

Chemical purification of tungsten ore. Y. MORI, T. MORI, AND NIPPON JÔSEKI SEIREN Co. Japan 36, 607, June 18, 1920. A mixt. of 100 parts powdered wolframite (or scheelite), 20 parts Zn dust, 20 parts Al or Mg, 5 parts  $\text{SiO}_2$ , and 4 parts  $\text{BaO}_2$  is placed in a graphite crucible, on which 5 parts  $\text{KClO}_4$  are placed and fired. A product contg. 80-90% metallic W is formed.

Apparatus for purification of zinc. UMATARÔ HATTORI. Japan 36,823, July 24, 1920.—Mixed vapors of Zn, Fe, Sn, Pb, Cu, etc., produced by heating Zn ore or Zn compds. in a retort are conducted to a sepg. chamber, in which metallic vapor condenses and comes back to the retort, while Zn proceeds into a condenser, producing metallic Zn of 99.95% purity.

Aluminium alloy. I. YAMAMURA AND NIPPON KEIGIN KÔGYÔ Co. Japan 36,657, June 25, 1920.—97.34 parts Al are heated to  $900^\circ$  in a crucible with 79 parts Ni with agitation. The temp. is gradually lowered to  $630^\circ$ , at which point 13 parts Sn and 51 parts Mg are added. The whole is melted and completely mixed. The alloy is not affected by boiling with sea-water or 50%  $\text{AcOH}$  for 1.5 hrs.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

Proust as an organic chemist. EDUARD FÄRBER. *Z. angew. Chem.* **34**, Aufsatzteil, 245-6(1921). E. H.

Ludwig Knorr. WILHELM SCHNEIDER. *Chem. Ztg.* **45**, 600-10(1921).—Obituary. E. H.

Synthesis of hexamethylenetetramine. WALTHER HERZOG. *Z. angew. Chem.* **33**, Aufsatzteil, 48(1920).— $\text{CO}_2$  is passed into  $(\text{NH}_4)_2\text{CO}_3$  soln., giving the bicarbonate. Impure carbonate is used so that a large amt. of ammonium carbonate also is present.  $\text{HCHO}$  soln. is then added and the mixt. distd. from a water bath under reduced pressure, hexamethylenetetramine distg. off. The existence of an intermediate product is mentioned— $\text{NH}_4\text{HCO}_3 + \text{NH}_2\text{CO}_2\text{NH}_4 = \text{C}_2\text{H}_{10}\text{O}_2\text{N}_2$  and  $4\text{C}_2\text{H}_{10}\text{O}_2\text{N}_2 + 18\text{CH}_3\text{O} = 3\text{C}_4\text{H}_{12}\text{N}_4 + 8\text{CO}_2 + 22\text{H}_2\text{O}$ . A 10% excess of  $(\text{NH}_4)_2\text{CO}_3$  is used on account of the instability of the bicarbonate, the yield being 66% based on the amount of  $\text{HCHO}$  used. The product is obtained cryst. by crystn. from abs. alc. or by vacuum sublimation. H. W. POST

Brodie's hydrocarbon melene,  $\text{C}_{20}\text{H}_{40}$ . Y. FUNCKE. *Arch. Pharm.* **259**, 93-101 (1921).—The purpose of the investigation was mainly to check the findings of Brodie relative to the hydrocarbon  $\text{C}_{20}\text{H}_{40}$  (cf. *Ann.* **71**, 144). A summary of F.'s results is as follows: 1. In the ordinary dry distn. of beeswax, a mixt. of satd. and unsatd. hydrocarbons is obtained, which is contaminated to some extent with O-containing substances. In the lower boiling fractions unsatd. hydrocarbons preponderate, while in the higher boiling portions the conditions are exactly reversed. 2. The rapidity with which the distn. is carried out is determinative for the quantity of high mol. hydrocarbons, a rapid distn. giving the highest yield in this respect. 3. The solid hydrocarbons thus obtained can on treatment with cold  $\text{Et}_2\text{O}$  be divided into 2 groups, one of which is characterized by hydrocarbons containing about 25 C atoms, the other about 30. The sepn. of the members of either group is a matter of great difficulty owing to their marked physical similarity. It is shown that the elementary analysis, upon which



Brodie based his conclusions on insufficient for detg. the particular hydrocarbon in question, that the substance or rather material to which Brodie gives the name melene is not a compd. in fact but a mixt. of satd. and unsatd. hydrocarbons with about 30 C atoms, that finally, while the presence of the unsatd. hydrocarbon  $C_{30}H_{48}$  in this mixt. cannot be questioned, its isolation in pure condition has so far not been effected and this hydrocarbon should, therefore, be stricken from the chem. literature. W. O. E.

**Preparation of glyoxal by the action of acetylene on gold chloride or gold bromide.** KARL KINDLER. Univ. Hamburg. *Ber.* 54B, 647-9(1921).—The Au is quant. pptd. by  $C_2H_2$  from aq. solns. of its halides containing not much more than 1.5% Au; the org. products are only glyoxal and small amts. of  $CO_2$ ; the finely divided Au can again readily be converted into its halides by means of Cl or Br. The  $C_2H_2$ , purified according to Götting's directions (*Ber.* 32, 1877(1899)) and, to free it from any AcH which might have been formed, further washed with 30%  $NaHSO_3$  and then with 30% NaOH, was passed into 2.8 g. of the Au halide in 100 cc.  $H_2O$  at 70-80° in a flask connected with a condenser, cooled receiver and NaOH wash bottle protected from atm.  $CO_2$  with soda-lime. With a moderate stream of  $C_2H_2$ , the reaction is complete in about 2 hrs. The yield of  $CO_2$  was about 12%; no AcH could be detected in the receiver. The filtrate from the pptd. Au with  $PbNH_4$  in dil. AcOH gave 88% of glyoxal osazone, m. 169-70°.

CHAS. A. ROUILLER

**Dithiocarbazinic acid.** SIMA M. LOSANITCH. Univ. Belgrade. *J. Chem. Soc.* 119, 763-5(1921).—Ammonium dithiocarbazinate,  $H_2NNHCSSNH_4$ , is obtained when an alc. soln. of  $N_2H_4 \cdot H_2O$  containing a large excess of  $NH_3$  is slowly treated, with cooling, with the corresponding quantity of  $CS_2$ , yellow transparent prisms, m. and decomp. 114°. Methyl ester,  $H_2NNHCSSMe$ , by treating the  $NH_4$  salt in dil. alc. with 1 mol. MeI, needles or prisms, m. 82°. 2 mols. MeI gives methyl bismethyldithiocarbamate,  $(SMcCSNMe)_2$ , also formed by the action of MeI on the Me ester, needles, m. 118-9°. Methylammonium dithiocarbazinate,  $H_2NNHCSSNH_2Me$ , yellow needles, m. 112° (decompn.). Hydrazine phenyldithiocarbazinate,  $NHPhNHHCSSNH_2$ , decomp. 110°. When heated with acids, the dithiocarbazates decomp. into their components.

C. J. WEST

**Condensation of methylene dicyanide with ketones and aldehydes.** G. J. ÖSTRÖM. *Öfversigt Finska Vetenskaps Soc. Förhändl.* 57A, No. 11, 13 pp.(1915).—An investigation of the condensations of methylene dicyanide with ketones and aldehydes. Methylene dicyanide and acetone in mol. proportions give, in presence of a little piperidine, a colorless, cryst. substance,  $C_4H_4N_4$ , volatile at 400°, easily sol. in NaOH and KOH. Condensation of methylene dicyanide with a large excess of acetone (in alc.,  $Et_2O$  or  $H_2O$ ) gives clear crystals which, when heated with concd. HCl in a bomb tube at 150° for 5-6 hrs., give an acid,  $C_4H_4O_4N_4$ , yellow needles, m. 152-3°. From the portion of the condensation products melting at lower temp., a cryst. acid could be extd. by KOH. Other condensation products were obtained with  $MeCOEt$ ,  $CH_3Ac$ , and  $Et_3CO$ . Condensation with  $BzH$  in alc. gives a compd.,  $CHPh:C(CN)_2$ , m. 88°. With  $CH_2O$  in water, plates, m. 206-7°, of a probable polymeride of the formula  $CH_2:C(CN)_2$  were obtained. With AcH needles of a substance,  $CHMe:C(CN)_2$ , m. 77-8° (from alc.), were obtained.

J. C. S.

**Formation and stability of spiro compounds. IV. Ketones derived from open-chain and cyclic glutaric acids.** GEORGE ARMAND ROBERT KON. Imperial Coll. Sci. Tech. *J. Chem. Soc.* 119, 810-30(1921); cf. C. A. 15, 1018.—K. deals with the factors affecting the closing and disruption of 4-membered C-rings, in particular of rings which may be described as extra-annular. The 2 methods which are of primary importance are: the distn. of the Ca salts of dibasic acids and the elimination of alcs. from esters of dibasic acids. Those acids which can be converted into ketones do



not yield anhydrides under the usual exptl. conditions, and *vice versa*. In each case the limiting conditions appear to lie between those which hold in glutaric and in adipic acid. In order to ascertain the limiting conditions with any degree of accuracy the investigation of compds. having intermediate stabilities is required. The *gem*-substituted glutaric acids (Ingold, *C. A.* 15, 1696) occupy various positions between glutaric and adipic acids in the scale of stability of the ketones to which they should give rise. The present investigation deals with the complete investigation of the products formed when the Ca salts of these acids are distd. The arithmetical figures obtained from the formula given in *C. A.* 15, 1018, for the instabilities of the ketones corresponding with the normal-chain dibasic acids are as follows: succinic, 0.927; glutaric, 0.436; adipic, 0.126; pimelic, 0.084; suberic, 0.203; azelaic, 0.313. The figure 0.436 represents a ketone too unstable to survive the conditions of a Ca salt distn., while a ketone of instability 0.126 is sufficiently stable to be prepd. in this way. The critical figure lies somewhere within the range 0.436 and 0.126. The substituted glutaric acids have the following values: cyclopentanediactic acid, 0.344; dimethylglutaric acid, 0.339; cyclohexanediactic acid, 0.301; cycloheptanediactic acid, 0.266. Since it is shown that, although the cyclic ketones are undoubtedly the products first formed when the Ca salts of the  $\beta,\beta$ -disubstituted glutaric acids are distd., none of them survives the exptl. conditions, consequently the figure for the critical stability governing this reaction must lie within the narrower range 0.266 to 0.126. The Ca salts were prepd. by dissolving 1 g.-mol. in dil.  $\text{NH}_4\text{OH}$ , boiling off the excess  $\text{NH}_3$  and pouring the soln. on to a paste from 100 g. slaked  $\text{CaO}$ . The mixt. is evapd. to dryness, the salt powdered, dried at  $100^\circ$ , and then distd. in a stream of  $\text{N}_2$ . 1 g.-mol. of  $\beta,\beta$ -dimethylglutaric acid gave 70–80 g. distillate, from which were isolated:  $\text{Me}_2\text{CO}$ , 30%; mesityl oxide, 5%; isophorone, 33%; and an unsatd. hydrocarbon, isobutylene (?).  $\beta,\beta$ -Diethylglutaric acid gave about 90 g. distillate, composed of:  $\text{Me}_2\text{CO}$ , 16%;  $\beta$ -ethyl- $\Delta^2$ -butylene,  $\text{Et}_2\text{C}=\text{CH}_2$ , mobile liquid, b.  $67\text{--}8^\circ$ ,  $d_{20}^{20}$  0.69403,  $n_D^{20}$  1.40276,  $[\text{R}_L]_D$  29.55 (dibromide,  $b_{71}$  108–10°, which yielded an aldehyde on boiling with  $\text{H}_2\text{O}$ );  $\text{Et}_2\text{CO}$ , in 5% yield; a ketone,  $\text{Et}(\text{MeCH}_2)\text{CCH}_2\text{COMe}$  (?), liquid with odor of isophorone and mesityl oxide,  $b_{71}$  164–6°,  $d_{15.4}^{15.4}$  0.85444,  $n_D^{15.4}$  1.44241,  $[\text{R}_L]_D$  38.83. Semicarbazone, silky, flattened needles, m.  $145\text{--}6^\circ$ . Oxime,  $b_{19}$  118–9°. Reduced, it gave the ketone  $\text{C}_8\text{H}_{16}\text{O}$ , isolated as the semicarbazone, long flattened needles, m.  $141\text{--}2^\circ$ . The yield, of this fraction was 25%. A high-boiling fraction, corresponding to about  $\text{C}_{10}\text{H}_{18}\text{O}$ , b.  $240\text{--}60^\circ$ , was obtained, but no definite compd. was isolated. Cyclopentanediactic acid gave 90 g. of a dark green distillate, which gave 20%  $\text{Me}_2\text{CO}$ , 6% methylenecyclopentane (*Ann.* 347, 325), a little cyclopentanone, and about 33% cyclopentanylacetone,  $\text{C}_5\text{H}_7\text{CH}_2\text{COMe}$ ,  $b_{24}$  181–1°,  $d_{21.1}$  0.9294,  $d_{15.4}$  0.9332,  $n_D^{24.3}$  1.4650,  $n_D^{19.4}$  1.46728,  $[\text{R}_L]_D$  36.91. Semicarbazone, which is sep'd. into 2 forms by crystn. from  $\text{MeOH}$ , less sol. form, fan-shaped aggregates from  $\text{MeOH}$  or  $\text{EtOH}$ , decomp.  $189^\circ$ ; more sol. form, rosettes of small crystals, m.  $138^\circ$ . Upon reduction cyclopentylacetone is formed,  $b_{24}$  179°, with the odor of  $\text{AmOAc}$ ,  $d_{20}$  0.9022,  $n_D^{23}$  1.44452,  $[\text{R}_L]_D$  37.15; semicarbazone, glistening plates, m.  $171\text{--}1.5^\circ$ , long flattened needles from  $\text{MeOH}$ . The highest boiling fraction,  $b_{11}$   $140\text{--}2^\circ$ , corresponded to  $\text{C}_{10}\text{H}_{18}\text{O}$ , but no definite compd. has been isolated. Cyclohexanediactic acid gave 96 g. distillate, composed of 12–15%  $\text{Me}_2\text{CO}$ , about 11% methylenecyclohexane (*Ann.* 347, 329) and about 30% cyclohexenylacetone (*C. A.* 7, 1002). Cycloheptanediactic acid gave 24 g. distillate from 55 g. acid. This contained a small amt.  $\text{Me}_2\text{CO}$ , about 16% of methylenecycloheptane (*Ann.* 314, 158); cycloheptenylacetone,  $b_{71}$  223–5°,  $d_{21.1}$  0.9396,  $n_D^{21.3}$  1.47917,  $[\text{R}_L]_D$  45.92. Semicarbazone, spherical clusters of needles, m.  $166.5\text{--}7^\circ$ . A small quantity of a lower melting form was obtained, m.  $96^\circ$  (decompn.). Glutaric acid yielded only 26 g. distillate, from which  $\text{Me}_2\text{CO}$  and a little cyclohexanone were isolated. No



trace of unsatd. ketones could be isolated and the decompn. appears to be of a deep-seated character.  $\beta$ -Methylglutaric acid gave 42 g. distillate. 15%  $\text{Me}_2\text{CO}$  were isolated, a small amt. of  $\text{MeCOPr}$ , some 3-methylcyclohexanone, and some *m*-cresol.

C. J. WEST

The influence of ammonium molybdate upon the rotatory power of malic acid. F. DARMOIS. *Compt. rend.* **171**, 348-50 (1920).—Gernez (*Compt. rend.* 1887) has shown in a series of extensive researches that the alkali molybdates and tungstates greatly increase the relatively slight rotatory powers of tartaric and malic acids in  $\text{H}_2\text{O}$ , and he explained these phenomena by a hypothesis involving the formation of a compd. between the acid and the salt; but neither he nor subsequent investigators were able to isolate such compds. D., in a study of the malic acid- $\text{NH}_4$  molybdate mixt., has succeeded in isolating a compd. whose optical activity is of such magnitude as to explain the large increase in rotatory power of these solns. The exact compn. of this compd. is not stated.

CHARLES F. RUBY

Chemistry of uric acid. I. Introduction. HEINRICH BILTZ. *Ann.* **423**, 119-22 (1921).—The following papers conclude an extensive investigation of the chemistry of uric acid, treating specially of the 4,5-double bond. References are given to descriptions of all the uric acids prepd. since Fischer's book (cf. also *Ber.* **32**, 435). II. 7-Methyluric acid and its derivatives. HEINRICH BILTZ, KARL MARWITZKY AND MYRON HEYN. *Ibid.* 122-45.—The most suitable prepn. of 7-methyluric acid (A) is given in Ger. Pats. 102,158 and 105,345. It is modified so that 200 g. uric acid suspended in 2 l.  $\text{H}_2\text{O}$  are dissolved in 200 g. KOH in 500 cc.  $\text{H}_2\text{O}$ , treated with 300 g. 40%  $\text{HCHO}$  and acidified after 1 day with  $\text{HCl}$ . After shaking 12 hrs. the product is filtered and 50 g. of the crude hydroxymethyluric acid in 1250 cc. concd.  $\text{HCl}$  are reduced at  $45^\circ$  with 350 g. Sn, the operation requiring 12-14 days. A may also be prepd. by treating 13 g. 7-methyluramil with a boiling soln. of 10 g.  $\text{KCN}$  in 46 cc.  $\text{H}_2\text{O}$  for 0.5 hr., acidifying with 175 cc. 20%  $\text{HCl}$ , and then heating for 1 hr. Preps. from various sources were identical in chem. properties and crystal form. While the first method uses materials which are more accessible, the 2nd is more rapid. The true soly. of A in boiling  $\text{H}_2\text{O}$  is detd. as 1:199, but supersatd. solns. are easily prepd. Monoacetyl-7-methyluric acid,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_4$ , by boiling 1 g. A and 150 cc.  $\text{Ac}_2\text{O}$  until soln. resulted, lancet-like, pointed leaflets from  $\text{H}_2\text{O}$ , which decomp. above  $315^\circ$ . It gave the murexide reaction. 7-Methyluric acid glycol dimethyl ether,  $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_4$ , prepd. by passing Cl into a mixt. of 2 g. finely powdered A in 10 cc.  $\text{MeOH}$  cooled in ice and salt, compact 4- or 6-sided prisms from  $\text{H}_2\text{O}$  or  $\text{MeOH}$ , m.  $211^\circ$  (decompn.). It is sol. in about 9 parts  $\text{MeOH}$ .  $\text{SnCl}_2$  and  $\text{HCl}$  reduce it to A. Diethyl ether, as above, using  $\text{EtOH}$ , rhombic leaflets from  $\text{EtOH}$ , m.  $214-5^\circ$  (decompn.). It is sol. in about 35 parts  $\text{EtOH}$ , less so in  $\text{H}_2\text{O}$ ,  $\text{AcOH}$ ,  $\text{AcOEt}$  and scarcely sol. in  $\text{Et}_2\text{O}$ . 7-Methyl-1-hydroxy-5-ethoxy-4,5-dihydrouric acid (7-methyluric acid glycol ethyl hemiether), (D),  $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4$ , crystals from a soln. of 1 g. C in 10 cc. warm dil.  $\text{HCl}$ , prisms or small leaflets from  $\text{EtOH}$ , m.  $214^\circ$ . Reduced with  $\text{H}_2$ , it yields 1-methylhydantoin. Methyl 1-methyl-5-methoxyhydantoin carbonate,  $\text{C}_7\text{H}_{10}\text{O}_5\text{N}_4$ , is formed by passing Cl through a mixt. of 2 g. B and 20 cc.  $\text{MeOH}$  at room temp., long rhombic tables from  $\text{MeOH}$ , m.  $131^\circ$ .  $\text{HI}$  reduces this to 1-methylhydantoin. Attempts to prep. 1-methylspirodihydantoin by heating with  $\text{CONH}_2$  in the presence of  $\text{HCl}$  were unsuccessful, as were also those to prep. 7-methyluric acid glycol by the action of Cl upon A in  $\text{H}_2\text{O}$ . 7-Methyl-5-chloro- $\Delta^{4,5}$ -isouric acid,  $\text{C}_8\text{H}_7\text{O}_5\text{N}_4\text{Cl}$ , is obtained by passing dry Cl into a cooled mixt. of 1 g. A, 8 cc. glacial  $\text{AcOH}$  and 2 cc.  $\text{Ac}_2\text{O}$ ; soln. results in 6 min. The hygroscopic acid forms compact prisms which decomp. above  $200^\circ$ . Reduction with  $\text{SnCl}_2$  and  $\text{HCl}$  gave A.  $\text{Alc}$ . gives the corresponding ethers B or C.  $\text{H}_2\text{O}$  decomp. the acid into a mixt. of alloxan and methylurea, which form an addition product, m.  $137^\circ$ . 7-Methyl-5-chloropseudouric



acid,  $C_8H_7O_4N_2Cl$ , by passing Cl into a mixt. of 5 g. 7-methylpseudouric acid (E) and 35 cc. AcOH, leaflets with 1 AcOH, decomp.  $177^\circ$ . Reduced with  $SnCl_2$  and HCl it gives E. The action of  $H_2O$  gave the above mixt. of alloxan and methylurea, which, if allowed to stand overnight, yields 9-methyluric acid glycol. With MeOH at room temp., 7-methyl-5-methoxypseudouric acid is formed, best prepd. by the action of Br upon 1 g. E in 5 cc. MeOH, 6-sided tables, m.  $176^\circ$  (decompn.). 5-Ethoxy derivative, leaflets, decomp.  $165^\circ$ . Upon crystn. from dil. HCl, D is formed. III. 7-Ethyluric acid and its derivatives. *Ibid* 147-59.—Both 7-ethyluric acid (A) and 7-ethylpseudouric acid (B) may be synthesized from 7-ethyluramil (C) according to Fischer. C was prepd. from alloxantin (Piloty, *Ann.* 333, 64(1904)) or from dialuric acid with an excess of  $EtNH_2$ . If 1.5 mols.  $EtNH_2$  are used, dialuric acid ethyl amine,  $C_8H_{11}O_4N_2$ , results, m.  $286^\circ$ , soly. in boiling  $H_2O$  about 1 in 35. C is best prepd., however, by Biltz and Heyn's method (*C. A.* 11, 2197). 7-Ethylpseudouric acid,  $C_7H_9O_4N_2$ , from 10 g. C and 10 g. KCNO in 30 cc.  $H_2O$  by warming 0.5 hr., 4-sided prisms with 1  $H_2O$ , m.  $208^\circ$  (decompn.). It is sol. in 17 parts boiling  $H_2O$ . 7-Ethyluric acid,  $C_7H_9O_4N_2$ , prepd. from B as usual, needles, decomp.  $361-2^\circ$ . 7-Ethyluric acid glycol dimethyl ether,  $C_9H_{11}O_4N_2$ , by passing Cl into a mixt. of 5 g. dry A and 40 cc. dry MeOH with cooling, small nearly quadratic plates, m.  $206^\circ$  (decompn.).  $SnCl_2$  and HCl reduce it to A. Diethyl ether,  $C_{11}H_{15}O_4N_2$ , fine needles, m.  $193^\circ$  (decompn.). The soly. in boiling alc. is about 50. 7-Ethyl-4-hydroxy-5-ethoxy-4,5-dihydrouric acid (7-ethyluric acid glycol ethyl hemiether) (D),  $C_9H_{11}O_5N_2$ , obtained if a small amt. of  $EtOH$  is used, compact, lancet-like leaflets, m.  $208^\circ$ . It is reduced to 1-ethylhydantoin, m.  $104^\circ$  (Heintz, *Ann.* 133, 65, found  $100^\circ$ ). Methyl 1-ethyl-5-methoxyhydantoin carbonate,  $C_7H_{12}O_5N_2$ , by evapg. a soln. of 6 g. di-Me ether in 30 cc. satd.  $MeOH-HCl$ , large tables, m.  $146^\circ$ . Upon reduction this gives a good yield of 1-ethylhydantoin. Attempts to prep. 7-ethyl-5-chlorouric acid and the 5-chloropseudo acid failed. 7-Ethyl-5-methoxypseudouric acid,  $C_7H_9O_4N_2$ , prepd. by the action of excess Br upon 0.5 g. B in 4 cc. abs. MeOH, leaflets, decomp.  $167-8^\circ$ . 5-Ethoxy derivative,  $C_9H_{11}O_4N_2$ , lancet-like leaflets, decomp. about  $118-20^\circ$ . Crystd. from dil. HCl D is formed. 7-Ethyluric acid glycol hypochlorite,  $C_7H_9O_5N_2Cl$ , by passing a lively stream of Cl into a suspension of A in  $H_2O$ , rhombic tables decomp.  $163^\circ$ . When heated with  $EtOH$ ,  $HClO$  is split off, but a cryst. product was not obtained. With concd. HCl this evolves Cl and forms 1-ethylcapfolide,  $C_7H_7O_3N_2$ , compact, rhombic tables, m.  $210-2^\circ$ . IV. Derivatives of 7,9-dimethyluric acid. HEINRICH BILTZ AND HANS RÜLOW. *Ibid* 159-77.—7,9-Dimethyluric acid (A) was prepd. according to Fischer (*Ber.* 30, 2209; 32, 463) with slight modifications. 1 g. dissolves in about 430 g. boiling  $H_2O$ . Upon oxidation this yields 7,9-dimethyluric acid glycol (B) (Fischer, *Ber.* 17, 1781) which has been compared with the synthetic product (Biltz, *C. A.* 4, 2644) and the complete identity of the 2 established. Dimethyl ether,  $C_9H_{11}O_4N_2$ , by the action of Cl upon 5 g. A in 50 cc. abs. alc., rhombic or 6-sided leaflets, decomp.  $187^\circ$ . Diethyl ether,  $C_{11}H_{15}O_4N_2$ , rhombic leaflets, decomp.  $193^\circ$ . Boiled with dil. HCl, the Me ether gives the methyl hemiether,  $C_9H_{11}O_5N_2$ , 6-sided tables, m.  $184^\circ$ . Reduced with HI it gives 1,3-dimethylhydantoin, and sapond. with concd.  $H_2SO_4$ , B. The ethyl hemiether,  $C_9H_{13}O_5N_2$ , flat 4-sided prisms, m.  $185^\circ$ . Methyl 1,3-dimethyl-5-methoxyhydantoin-5-carboxylate,  $C_9H_{13}O_6N_2$ , by the action of  $MeOH-HCl$  upon the di-Me ether, compact, thick prisms, m.  $72^\circ$ . Heating with  $CO(NHMe)_2$  gives tetramethylspirodihydantoin (*C. A.* 5, 1446). The corresponding Et deriv. could not be obtained. 7,9-Dimethyluric acid 4,5-dichloride,  $C_7H_7O_3N_2Cl_2$ , by the action of Cl upon 5 g. A in 50 cc. dry  $CHCl_3$ , decomp.  $126-30^\circ$ . Cold  $H_2O$  gives B.  $EtOH$  gives the di-Et ether,  $MeOH$  the di-Me ether. On reduction A was formed. A in alk. soln., shaken with  $Me_2SO_4$ , gives 1,7,9-trimethyluric acid. V. Derivatives of 1,7,9-trimethyluric acid. HEINRICH BILTZ AND



HANS KRZIKALLA. *Ibid* 177-84.—1,7,9-Trimethyluric acid (A) was prepd. by the action of 7 g.  $\text{Me}_2\text{SO}_4$  upon 3 g. 7,9-dimethyluric acid and 5.2 g. KOH in 75 cc.  $\text{H}_2\text{O}$  (yield, 3.6 g.). Attempts to prep. the glycol (action of Cl in  $\text{H}_2\text{O}$  suspension) gave allocaffeine, m. 204°. 1,7,9-Trimethyluric acid 4,5-glycol dimethyl ether,  $\text{C}_{10}\text{H}_{16}\text{O}_4\text{N}_4$ , by passing Cl into a suspension of 5 g. A in 45 g. abs. MeOH, 6-sided tables, m. 152°. Upon reduction with HI or Na-Hg, it yields A. Diethyl ether,  $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_4$ , rhombic or 6-sided tables, m. 169°. Attempts to prep. the hemiether or the pseudo acid always gave trimethylcaffolide. Chlorination in an indifferent solvent ( $\text{CHCl}_3$ ) gives the dichloride, though this could not be isolated. VI. The preparation of 1,3-dimethylpseudouric acid and 1,3-dimethyluric acid. HEINRICH BULTZ AND MYRON HEYV. *Ibid* 185-92.—200 g. tech. uric acid are mixed with 1600 cc. glacial AcOH to a thick paste, 20 cc.  $\text{H}_2\text{O}$  added and Cl is passed in rapidly. After 2-3 min. the mixt. is cooled with ice water (5-10°). After 15-25 min. crystals of 5-chloropseudouric acid begin to sep. The Cl is interrupted, 200 cc. AcOH added and the mixt. allowed to stand about 1 hr. (disappearance of the uric acid detd. by examn. under the microscope) and the excess of Cl removed with a stream of air. The mixt. is now cooled to 5° and a soln. of 350 g. cryst.  $\text{SOCl}_2$  in 350 cc. concd. HCl added slowly. After 3-4 hrs. it is dild. to twice its vol. with dil. HCl and after 1 hr. at 0°, filtered. The yield is 150 to 180 g. Purified through the Na salt, 20-30 g. are lost. Upon methylating 50 g. of the pseudo acid in 50 g. NaOH and 400 cc.  $\text{H}_2\text{O}$  with 150 g.  $\text{Me}_2\text{SO}_4$  (400 g. ice are added) by shaking 0.75 hr. 35 g. 1,3-dimethylpseudouric acid are obtained. When this is heated with concd. HCl, 1,3-dimethyluric acid is formed. It is not necessary to isolate the pseudo acid. The filtrate is acidified, concd. half, an equal vol. of concd. HCl added and the soln. boiled. Uric acid, methylated as above, gives a product rich in 1,3-dimethyluric acid since 2 g. of the product gave 1.5 g. of the glycol di-Me ether. VII. Methylation of 7-methylpseudouric acid and 7-ethylpseudouric acid. HEINRICH BULTZ AND GERTRUD ZELLNER. *Ibid* 192-200.—5 g. 7-methylpseudouric acid (see above), treated in alk. soln. with 16 g.  $\text{Me}_2\text{SO}_4$ , gave 6 g. of the sodium salt of 1,3,7-trimethylpseudouric acid, flat, broad prisms, decomp. about 80°. Acidified, 6 g. Na salt in concd.  $\text{H}_2\text{O}$  soln. gave 3 g. free acid. 1,3,7-Trimethyl-5-chloropseudouric acid,  $\text{C}_8\text{H}_{10}\text{O}_4\text{N}_4\text{Cl}$ , by the action of Cl upon the carefully dried free acid in a mixt. of AcOH and  $\text{Ac}_2\text{O}$ , 4-sided leaflets, decomp. 180°. With dry EtOH, this gives the ethoxy derivative, fine needles, decomp. 145°. Reduction with HI gave 1,3,7-trimethyluric acid, while Na-Hg gave the pseudo acid. 1,3-Dimethyl-7-ethyluric acid is formed by the methylation (with  $\text{Me}_2\text{SO}_4$ ) of 7-ethylpseudouric acid, flat prisms, m. 288°. 1,3-Dimethyl-7-ethyluric acid 4,5-glycol dimethyl ether, tables, m. 189°. VIII. 8-Thiouric acid and isoxanthine with alkyl in position 9. HEINRICH BULTZ, KARL STRUVE, ERNST TOPP, MYRON HEYV AND RUDOLF ROBL. *Ibid* 200-26.—9-Methyl-8-thiopseudouric acid (A),  $\text{C}_8\text{H}_9\text{O}_2\text{N}_2\text{S}$ , by treating a soln. of 14.3 g. uramil in 100 cc. 2 N NaOH with 9.5 g. MeNCS for 15 hrs., dild. with  $\text{H}_2\text{O}$  and acidifying with HCl, 6-sided tables, decomp. about 190°. Soly. in boiling water is about 7.5, in boiling alc. about 1. The attempt to prep. 8-thiopseudouric acid was unsuccessful. 9-Methyl-8-thiouric acid,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_2\text{S}$  (B), by boiling the Na salt of A with concd. HCl, fine flat needles, decomp. above 350°. The addition of 40 g. pulverized  $\text{NaNO}_2$  to a mixt. of 15 g. B and 60 cc. 6 N HCl during 5 hrs. gave II g. 9-methyl- $\Delta^{7,8}$ -isoxanthine (C),  $\text{C}_8\text{H}_9\text{O}_2\text{N}_4$ , thin lancet-like leaflets, decomp. 383°. The action of 15 g.  $\text{NaNO}_2$  upon 6.6 g. B and 150 cc. 7 N HCl at 50°, followed by satn. with  $\text{NH}_3$ , gave orange-red, glistening leaflets,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_4$ , which lose  $\text{NH}_3$  at 105°. This may be an ammonium salt of a nitroso derivative. Silver salt, flocculent. 9-Methyl-8-bromo- $\Delta^{7,8}$ -isoxanthine (D), isolated as the perchlorate,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_4\text{Br} \cdot \text{Br} \cdot \text{H}_2\text{O}$ , when 5 g. C are warmed with 100 cc. AcOH and 5 cc. Br 1 hr. on a boiling  $\text{H}_2\text{O}$  bath. Concd.  $\text{NH}_4\text{OH}$  gave the ammonium salt,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_4\text{Br} \cdot \text{NH}_4\text{H}_2\text{O}$ , fine



needles, which, acidified with HCl, gave the free base,  $C_8H_8O_2N_4Br$ , small crystals, turn brown at  $290^\circ$ . The Br atom is not reactive. 2,6-Dihydroxy-3,9-dimethyl- $\Delta^{7,8}$ -purine (3,9-dimethyl- $\Delta^{7,8}$ -isoxanthine),  $C_8H_8O_2N_4$ , is obtained by the methylation of C, long needles resembling caffeine, decomp.  $364^\circ$ . Chloroaurate, long needles, m.  $297-300^\circ$  (decompn.). In the bromination the new Me group is split off and D is formed. 9-Ethyl-8-thiopseudouric acid,  $C_7H_{10}O_2N_2S$ , from uramil and EtNCS, thin, pointed leaflets, m.  $185-90^\circ$  (decompn.). 9-Ethyl-8-thiouric acid, small leaflets, slowly decomp. above  $350^\circ$ . With  $NaNO_2$  and HCl this yields 9-ethyl- $\Delta^{7,8}$ -isoxanthine,  $C_7H_8O_2N_4$ , long felt-like needles, decomp.  $345^\circ$ . 1,9-Dimethyl-8-thiopseudouric acid, from 1-methyluramil and MeNCS, large 6-sided tables, decomp.  $204^\circ$ . 1,9-Dimethyl-8-thiouric acid, 4-sided prisms, decomp.  $370^\circ$ . 1,9-Dimethyl- $\Delta^{7,8}$ -isoxanthine,  $C_7H_8O_2N_4$ , glistening needles, decomp.  $350^\circ$ . Chloroaurate,  $C_7H_8O_2N_4 \cdot HAuCl_4$ , needles, decomp.  $255^\circ$ . 1-Methyl-9-ethyl-8-thiopseudouric acid, from 15.7 g. 1-methyluramil and 10 g. EtSCN in 80 cc. 2 N KOH, rhombic tables, decomp.  $195^\circ$ . 1-Methyl-9-ethyl-8-thiouric acid,  $C_8H_{10}O_2N_2S$ , glistening leaflets, decomp.  $367^\circ$ . 1-Methyl-9-ethyl- $\Delta^{7,8}$ -isoxanthine (2,6-dihydroxy-1-methyl-9-ethyl- $\Delta^{7,8}$ -purine),  $C_8H_{10}O_2N_4$ , needles, decomp.  $335^\circ$ . 1,3-Dimethyluracil, MeCNO and  $C_6H_6$ , heated 16 hrs. gave tetramethylhydantoinic acid (Ann. 221, 339). 34.2 g. dimethyluracil in 150 cc. 2 N KOH, shaken with 16 g. MeSCN, gave 47 g. 1,3,9-trimethyl-8-thiopseudouric acid,  $C_9H_{12}O_2N_2S$ , 4-sided prisms, decomp.  $208-9^\circ$ . Potassium salt. 1,3,9-Trimethyl-8-thiouric acid,  $C_9H_{12}O_2N_2S$ , needles, decomp.  $335^\circ$ . With HCl and  $NaNO_2$  this gives isocaffeine (1,3,9-trimethyl- $\Delta^{7,8}$ -isoxanthine),  $C_9H_{12}O_2N_4$ , fine needles, m.  $285-7^\circ$ . It may be sublimed like caffeine. Attempt to prep. the corresponding uric acid, by using  $AgNO_3$ ,  $H_2O$ ,  $Hg^{++}$  salts, etc. were unsuccessful. 1,3-Dimethyl-9-ethyl-8-thiopseudouric acid,  $C_9H_{12}O_2N_2S$ , 4-sided prisms, decomp.  $195^\circ$ . 1,3-Dimethyl-9-ethyl-8-thiouric acid,  $C_9H_{12}O_2N_2S$ , needles, m.  $277^\circ$  (decompn.). 1,3-Dimethyl-9-ethyl- $\Delta^{7,8}$ -isoxanthine,  $C_9H_{12}O_2N_4$ , fine needles, m.  $227-8^\circ$ . Phenyl-8-thiouric acid,  $C_{11}H_{10}O_2N_2S$ , poorly formed needles, decomp.  $300^\circ$ . The S could not be removed by the usual means. IX. Derivatives of 1,9-dimethyluric acid. HEINRICH BILTZ and KARL STRUPE. *Ibid.* 237-37.—The action of Cl upon a mixt. of 1,9-dimethyl- $\Delta^{7,8}$ -isoxanthine and AcOH gives 1,9-dimethyl-4-chloro- $\Delta^{7,8}$ -isouric acid (A), which is very hygroscopic.  $SuCl_2$  and HCl reduces this to 1,9-dimethyluric acid (B) (Ber. 32, 239). The chlorination of B gives A.  $H_2O$  acting upon A gives isopocaffeine. With MeOH 1,9-dimethyl-5-methoxypseudouric acid is formed, short, flat 4-sided prisms, decomp.  $203^\circ$ . This also results by passing Cl into a mixt. of B and MeOH. 5-Ethoxy derivative  $C_9H_{12}O_3N_2$ , long leaflets, decomp.  $290^\circ$ . Upon reduction either alkoxy deriv. yields 1,9-dimethylpseudouric acid,  $C_7H_{10}O_2N_2$ , needles, decomp.  $252^\circ$ . 3,9-Dimethyl-1-hydroxy-5-methoxy-1,5-dihydrouracil,  $C_8H_{12}O_3N_2$ , by acidifying a soln. of C in NaOH with HCl, or by shaking 3-methyluric acid glycol hemiether with  $Me_2SO$ , 4-sided prisms, m.  $204^\circ$ . The corresponding ethoxy compound,  $C_8H_{12}O_3N_2$ , forms long leaflets, m.  $174^\circ$ . X. Derivatives of 1-methyl-9-ethyluric acid. HEINRICH BILTZ and KARL STRUPE. *Ibid.* 237-41.—1-Methyl-9-ethyl-4-chloro- $\Delta^{7,8}$ -isouric acid,  $C_8H_8O_2N_2Cl$  (A), prepd. by passing Cl into a mixt. of 2 g. 1-methyl-9-ethylisoxanthine and 10 cc. AcOH, 6-sided tables, decomp.  $180^\circ$ . Reduced with HI, this gives 1-methyl-9-ethyluric acid (B), purified by pptn. from the  $NH_4$  salt with HCl, glistening needles, decomp. over  $360^\circ$ . The action of Cl upon B in AcOH gives A, dissolved with cooling in MeOH containing a little  $C_2H_5N$ , forms 1-methyl-9-ethyluric acid glycol dimethyl ether (C),  $C_{10}H_{14}O_3N_2$ , long rectangular leaflets, m.  $148^\circ$ . If A is dissolved without cooling 1-methyl-9-ethyl-5-methoxypseudouric acid,  $C_9H_{12}O_3N_2$ , is formed, long, 4-sided prisms, decomp.  $182^\circ$ . This may also be prepd. from C by soln. in a little HCl, or from B by the action of Cl in MeOH. 5-Ethoxy derivative, long leaflets, m.  $176^\circ$  (decompn.). XI. Derivatives of 1,3,9-trimethyluric acid. HEIN-



RICH BILTZ AND KARL STRUFE. *Ibid* 242-54. —The acid prepd. by Fischer and Ach's method contains some 1,3-di-Me acid. Pure 1,3,9-trimethyluric acid may be prepd. from trimethylisoxanthine. 1,3,9-Trimethyl-8-bromo- $\Delta^{3,8}$ -isoxanthine (bromo-isocaffeine), by the action of 23 g. Br upon a hot soln. of 25 g. isoxanthine in 75 g. AcOH, decomp. 256°. 8-Methoxy derivative, by boiling the Br deriv. with 10% MeOH-KOH, glistening needles, m. 230°. Upon warming with 20% HCl, this evolves MeCl and forms 1,3,9-trimethyluric acid (A), large, compact, glistening 4-sided prisms, decomp. 347°. The acid was also prepd. from 9-methylpseudouric acid, which, shaken with Me<sub>2</sub>SO<sub>4</sub> in NaOH soln., gave 1,3,9-trimethylpseudouric acid (B), rhombic tables, decomp. 220°; with concd. HCl, A results. 1,3,9-Trimethyl-4-chloro- $\Delta^{3,7}$ -isouric acid, by passing Cl into a cooled mixt. of 4 g. A and 20 cc. AcOH, small needles, m. about 170°. It decomp. quickly in the air. HI reduces it to A. MeOH gives 1,3,9-trimethyl-5-methoxypseudouric acid (C), long prisms, m. 184°. This was also prepd. by the action of Cl upon A or B in MeOH. 5-Ethoxy derivative, 6-sided prisms, m. 182° (decomp.). 1,3,9-Trimethyl-4-hydroxy-5-methoxy-4,5-dihydrouric acid, C<sub>7</sub>H<sub>11</sub>O<sub>5</sub>N<sub>3</sub>, was prepd. by the action of Me<sub>2</sub>SO<sub>4</sub> upon 1,3-dimethyluric acid glycol methyl hemiether or by pptg. a soln. of C in NaOH with HCl, long 4-sided prisms, m. 194°. 5-Ethoxy derivative, long leaflets, sinters 130°, m. 138°. XII. 3,9-Dimethyluric acid and its derivatives. HEINRICH BILTZ AND HANS KRZIKALLA. *Ibid* 255-81. —3,9-Dimethyluric acid (A), heretofore prepd. only through the Pb salt, may be obtained by the action of Me<sub>2</sub>SO<sub>4</sub> on the dry K salt. Dipotassium urate, by treating a paste of 100 g. crude uric acid and 700 cc. boiling H<sub>2</sub>O with a hot soln. of 100 g. KOH in 400 cc. H<sub>2</sub>O, cooling to 75°, adding 250-300 cc. alc., and then cooling further. After 2 days, it is dild. with 70% alc., and filtered. Yield, 110-120 g. 25 g. of this salt, finely pulverized, are heated with 45 g. Me<sub>2</sub>SO<sub>4</sub> and 120 cc. dry CCl<sub>4</sub> in a sealed tube at 130-40° for 6-8 hrs. The product was purified by crystg. from hot NH<sub>4</sub>OH. Monocetyl-3,9-dimethyluric acid by dissolving 4 g. A in 500 cc. Ac<sub>2</sub>O, needles, gradually decomp. above 300°. Me<sub>2</sub>SO<sub>4</sub> in alk. soln. gives tetramethyluric acid. Cl, passed into a MeOH suspension of A, gives 3,9-dimethyluric acid 4,5-glycol dimethyl ether (A'), C<sub>9</sub>H<sub>11</sub>O<sub>5</sub>N<sub>3</sub>, large prisms, decomp. 223°. Diethyl ether, large prisms, m. 238° (decomp.). Reduced with Na-Hg, A is formed. If HI is used, however, 1,9-dimethyluric acid is formed. At a lower temp. 1,9-dimethylpseudouric acid results. This transformation does not take place in the 3,7-series. 1,9-Dimethylpseudouric acid (B), treated with Me<sub>2</sub>SO<sub>4</sub>, gave the 1,3,9-trimethyl deriv. (see above). The action of HCl upon the dialkyl ethers gave the hemiethers described in Paper XI. The action of Cl upon 4 g. A in 40 cc. dry MeOH and the subsequent action of NH<sub>3</sub> upon the residue gave 3-methyl-5-methoxyhydantoinamide, C<sub>7</sub>H<sub>11</sub>O<sub>5</sub>N<sub>3</sub>, compact prisms, m. 208-210° (decomp.). By passing Cl into a mixt. of 2 g. B and 8 cc. glacial AcOH, 1,9-dimethyl-5-chloropseudouric acid, C<sub>7</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub>Cl, is formed, decomp. about 180°. With MeOH and EtOH this forms the corresponding alkoxo derivs. A mixt. of 3,9-dimethyluric acid and water, treated with Cl, gives the hypochlorous ester of 3,9-dimethyluric acid 4,5-glycol, decomp. 175°, unstable, giving off HClO by warming with alc. or H<sub>2</sub>O. With H<sub>2</sub>O the glycol is formed, C<sub>7</sub>H<sub>11</sub>O<sub>5</sub>N<sub>3</sub>, compact 4-sided prisms, decomp. 198.9°. Upon reduction it yields 3-methylhydantoin. 9-Methyluric acid glycol when heated with N NaOH gives off NH<sub>3</sub>, forming 3-methylcaffolide, C<sub>8</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub>, rhombic or 6-sided crystals, decomp. 220°. Upon warming a H<sub>2</sub>O soln., this loses CO<sub>2</sub> and forms 3-methyl-5-hydroxyhydantoinamide, C<sub>7</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub>H<sub>2</sub>O. The hydrate m. about 115-7°, the dried material at 178-80°. 1,7-Dimethylspiro-5,5-dihydantoin, C<sub>7</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub>, results by the action of Cl upon 3,9-dimethyluric acid in AcOH, by the action of H<sub>2</sub>SO<sub>4</sub> on the glycol, its hypochlorous ester or methyl hemiether, compact crystals, m. 264-5°. Silver salt. Methylation of the free hydantoin or the Ag salt gave tetramethylspirodihydantoin, m. 228°. XIII.



**Action of urea and substituted ureas upon alloxan and its methyl derivative.** HEINRICH BILTZ. *Ibid* 282-95.—The various known reactions are reviewed. The action of  $H_2O$  upon 1-methyl-5-chloropseudouric acid gives methylalloxan hydrate,  $C_4H_5O_4N_3$ ,  $H_2O$  and not the glycol (C. A. 11, 2202).  $MeNHCONH_2$ , acting on the hydrate at room temp., gave isopocaffeine. If  $HCl$  is added, a mixt. of isopocaffeine and 3,7-dimethyluric acid glycol is formed, sepd. by  $AcOEt$ . Attempts to combine alloxan with  $PhNHCONH_2$ ,  $CO(NHPh)_2$  or guanidine were fruitless. When 1 g. alloxan hydrate and 0.5 g.  $CS(NH_2)_2$  are dissolved in 1.5 cc.  $H_2O$ , a molecular compound is formed,  $C_5H_5O_4N_3S$ , 4-sided prisms, decomp. above  $150^\circ$ . XIV. 1,3-Diethylhydantoin. HEINRICH BILTZ AND FRITZ MAX. *Ibid* 295-6.—The reduction of 20 g. 7,9-diethyluric acid glycol with 60 g.  $HI$  on the  $H_2O$  bath, gave 6.2 g. diethylhydantoin,  $C_7H_{12}O_3N_2$ ,  $b_{714}$   $260-1^\circ$ . XV. 1,3,7,7-Tetramethyluramil. HEINRICH BILTZ AND GERTRAUD ZALLNER. *Ibid* 297-300.—1,3,7,7-Tetramethyluramil,  $C_8H_{12}O_4N_2$ , is prepd. by shaking 5 g. 7-methyluramil in 40 cc.  $H_2O$  (6 g.  $NaOH$ ) with 16 g.  $Me_2SO_4$ , compact tables, decomp.  $230-2^\circ$ . Monohydrate, fine, long pointed needles, decomp. about  $225^\circ$ . The same compd. is obtained by methylating 7,7-dimethyluramil, thus establishing the constitution. Perchlorate, tables. Nitrate, prisms. Hydrobromide, 6-sided prisms. XVI. Methylammonium iodide. HEINRICH BILTZ AND FRITZ MAX. *Ibid* 296-300.—Pure methylammonium iodide m.  $263-5^\circ$  (cf. Dunstan and Goulding, *J. Chem. Soc.* 71, 579). XVII. Derivatives of alloxanic acid. HEINRICH BILTZ AND FRITZ MAX. *Ibid* 301-17.—A list of all the previous derivs. is given with references. Me-5-methoxyhydantoincarboxylate (A) was prepd. according to Biltz and Heyn (C. A. 11, 2197) from methoxypseudouric acid by the action of  $MeOH-HCl$ . With  $Ba(OH)_2$  A gives Ba alloxanate. 5-Methoxyhydantoinylamide,  $C_5H_8O_4N_2$ , by the action of concd.  $NH_4OH$  on A at room temp., double pyramids with 1  $H_2O$  from  $H_2O$ , decomp.  $180-2^\circ$  when dry;  $Ba(OH)_2$  decomp. the product into  $CO(NH_2)_2$ ,  $CO(CO_2H)_2$ ,  $NH_3$  and  $MeOH$ . Upon reduction hydantoin was formed. 5-Methoxyhydantoinylmethylamide,  $C_6H_{10}O_4N_2$ , by the action of 33%  $MeNH_2$  upon A, short double pyramids or 6-sided tables, m.  $177-8^\circ$ . Ethylamide,  $C_{11}H_{14}O_4N_2$ , 4-sided prisms; monohydrate, m.  $84-5^\circ$ , anhydrous, m.  $136^\circ$ . 1-Methyl-5-methoxyhydantoinylamide, (C. A. 8, 3556) is also prepd. by the action of  $NH_4OH$  upon 1,3,7-trimethyl-5-methoxypseudouric acid. Reduction with  $HI$  gives  $NH_3$  and 1-methylhydantoin. Oxidation with  $K_2Cr_2O_7$  gave methylparabanic acid,  $C_6H_7O_4N_3$ , m.  $153^\circ$ . Methylation ( $Me_2SO_4$ ) gave 1,3-dimethyl-5-methoxyhydantoinylamide,  $C_8H_{14}O_4N_2$ , glistening 6-sided tables, m.  $201^\circ$ . 1-Methyl-5-methoxyhydantoinylmethylamide,  $C_9H_{16}O_4N_2$ , 6-sided tables, m.  $190^\circ$ . Ethylamide, compact prisms, m.  $139^\circ$ . 1,3-Dimethyl-5-methoxypseudouric acid, concd. in  $NH_4OH$  soln., gave 1,3-dimethyluric acid glycol Me hemiether. The action of  $NH_4OH$  for 1-2 min. upon 5-methoxypseudouric acid gave uric acid glycol Me hemiether, but the continued action gave 5-methoxyhydantoinyl amide. Uric acid glycol ethyl hemiether, rhombic or 6-sided tables decomp.  $208^\circ$ . 5-Ethoxyhydantoinylamide, decomp.  $225^\circ$ . XVIII. Alkylation of theobromine. HEINRICH BILTZ AND FRITZ MAX. *Ibid* 318-23.—Philips (*Ber.* 9, 1308) and Brunner and Leins (*Ber.* 30, 2584) obtained by the action of iodides upon the Ag salt of theobromine (A) high melting compds. Their results are not correct (van der Slooten, *Arch. Pharm.* 235, 471) as is shown by the present work. 10 g. A with  $MeI$  gave 3.5 g. pure caffeine. 8 g. A with 4.5 g.  $EtI$  heated in a sealed tube at  $100^\circ$  for 24 hrs. gave 2.1 g. ethyltheobromine, m.  $164^\circ$ .  $PrI$  gave 1.8 g. propyltheobromine (B), m.  $136^\circ$ . Hydrochloride, fine, hair-like needles 1-Propyl-3,7-dimethyluric acid 4,5-glycol dimethyl ether,  $C_{11}H_{16}O_4N_2$ , by the action of  $Cl$  upon B in  $MeOH$ , rhombic tables, sinter  $140^\circ$ , m.  $148^\circ$ . 1-Propyl-3,7-dimethyluric acid,  $C_{10}H_{11}O_4N_2$ , fine, glistening needles, m.  $233^\circ$ . 1-Butyltheobromine,  $C_{11}H_{15}O_4N_2$ , from 5 g. A and 3.5 g.  $BuI$ , fine glistening needles, m.  $119^\circ$ . Hydrochloride, fine, thread-



like crystals. *1-Butyl-3,7-dimethyluric acid 4,5-glycol dimethyl ether*, short, compact prisms, m.  $154^{\circ}$ . *1-Butyl-3,7-dimethyluric acid*, thin needles, m.  $270^{\circ}$ . C. J. WESR

The configuration of tartaric acid. J. BÖSEKEN AND J. COOPS. *Verslag Akad. Wetenschappen Amsterdam* 29, 368-74 (1920).—Measurements by the  $H_3BO_3$  method indicate that: (1) the  $CO_2$  groups repel each other more strongly than do the OH groups; (2) racemic acid and its active components are more strongly dissociated than mesotartaric acid. It is concluded from theoretical considerations that different as well as like groups in the same mol. may repel each other. A brief general discussion of the configuration of tartaric and succinic acids is given. JULIAN F. SMITH

Orientation of groups in the tartaric acids and the beginning of optical superposition. J. BÖSEKEN. *Verslag Akad. Wetenschappen Amsterdam* 29, 562-6 (1920).—Orientation studies by the  $H_3BO_3$  method showed that the OH groups in the active tartaric acids and some of their derivs. are closer together than in mesotartaric acid and its corresponding derivs. This is interpreted as indicating that the  $CO_2H$  groups, whether substituted or not, repel each other. These studies also showed that the OH groups repel each other. It is, therefore, probable that similar repulsive and attractive forces exist between all groups of the mol. A shift of any one would, therefore, change the relative positions of all. The work of van't Hoff, Patterson and Walden on optical superposition is briefly discussed. JULIAN F. SMITH

Determining the configuration of certain monosaccharides and of sucrose by the boric acid method. J. BÖSEKEN AND H. COUVERT. Delft-Deventer. *Verslag Akad. Wetenschappen Amsterdam* 29, 924-34 (1920).—The  $H_3BO_3$  method of studying configurations is applicable to compds. having at least 2 OH groups on adjacent C atoms and on the same side of the line joining the centers of the 2 C atoms. It is in general unsuited to compds. having several OH groups; but it is applicable to numerous sugars because they have a hydrofuran ring structure in which 2 adjacent C atoms may have OH groups on the same side of the ring. Configurations, based on this method, are given for  $\alpha$ -D-glucose,  $\alpha$ -D-galactose,  $\alpha$ -L-xylose,  $\alpha$ -L-arabinose,  $\alpha$ -D-mannose,  $\alpha$ -L-rhamnose and sucrose. Also in *Rec. trav. chim.* 40, 354-80 (1921). J. F. S.

The synthesis of sugars containing sulfur and selenium. FRITZ WREDE. *Z. physiol. Chem.* 112, 1-12 (1920); cf. C. A. 15, 1674.—*Dicellosyl selenide tetradecaacetate*,  $C_{40}H_{70}O_{24}Se$ , was prepd. by dissolving metallic K in alc., half satg. with dry  $H_2Se$  in the absence of O, and adding acetobromocellulose to the boiling soln. Slender, almost colorless needles, m.  $252^{\circ}$ , were obtained,  $[\alpha]_D^{25} - 47.08^{\circ}$  in  $CHCl_3$ . *Dicellosyl selenide*,  $C_{24}H_{40}O_{12}Se$ , was obtained from the Ac deriv. by sapon. the MeOH soln., with  $NH_3$  and extg. it with ether. It is a yellow powder which decomp. about  $215^{\circ}$ ,  $[\alpha]_D^{20} - 85.93$  to  $86.35^{\circ}$  in water. *Cellosyl glucosyl sulfide hendecaacetate*,  $C_{40}H_{70}O_{24}S$ , was prepd. by suspending a mixt. of acetobromocellulose and acetobromoglucose in 96% alc., and treating it with  $K_2S$ ; it crystallizes from MeOH as dense, rhombic platelets, m.  $163^{\circ}$ ,  $[\alpha]_D^{18} - 34.07^{\circ}$  and  $-34.19^{\circ}$  in  $CHCl_3$ . On treating the compd. with  $N$  NaOH, it was found that it contained 11 Ac groups. *Cellosyl glucosyl sulfide*,  $C_{14}H_{24}O_8S$ , was obtained from the Ac deriv. by treatment with  $NH_3$ ; it decomp.  $160^{\circ}$ ,  $[\alpha]_D^{14} - 46.73^{\circ}$  in water. The potassium salt,  $C_{15}H_{25}O_9SK_2$ , of the above compd. was prepd. by adding KOH to the trisaccharide in alc.; it decomp. about  $180^{\circ}$ . *Cellosyl glucosyl selenide hendecaacetate*,  $C_{40}H_{70}O_{24}Se$ , was prepd. in a similar way to the sulfide; it crysts. in rhombic platelets combined in rosets, m.  $141^{\circ}$ ,  $[\alpha]_D^{17} - 39.76^{\circ}$  and  $-40.36^{\circ}$  in EtOAc. On hydrolysis with  $NH_3$ , the *cellosyl glucosyl selenide*,  $C_{15}H_{25}O_9Se$ , was obtained as a yellow powder decomp. about  $160^{\circ}$ . *Galactosyl glucosyl selenide octaacetate*,  $C_{41}H_{70}O_{24}Se$ , was prepd. from acetobromoglucose and acetobromogalactose with alc.  $K_2Se$ , dense needles, m.  $161^{\circ}$ ,  $[\alpha]_D^{16} - 30.99$  to  $30.72^{\circ}$  in EtOAc. The compd. was obtained from the Ac deriv. by hydrolysis with  $NH_3$ ,  $[\alpha]_D^{16} - 48.35^{\circ}$



in water. Dicellosyl sulfide was degraded by acid and by emulsin hydrolysis.

J. C. S.

**Inner constitution of benzene and certain heterocyclic nuclei.** G. CIAMICIAN AND R. CIUSA. *Atti r. accad. Lincei* 30, 1, 72-4(1921).—On the basis of the results obtained by Angeli (*C. A.* 12, 365; 15, 523), various conclusions are drawn concerning the arrangement of the valencies in the mol. of benzene, pyridine, pyrrole, and thiophene.

J. C. S.

**Chloroiodo and iodoso derivatives.** A. PIERONI. Univ. Bologna. *Gazz. chim. ital.* 51, I, 47-8(1921).—On the supposition that iodoso derivs. may behave like nitroso derivs. P. has obtained a new type of compds.  $\text{PhNH}_2$  and  $\text{PhICl}_2$  were dissolved separately in the required mol. amts. in  $\text{C}_2\text{H}_5\text{N}$  and the latter soln. was poured into the former. A deep brown color appeared and heat was evolved. The liquid was evapd. on a watch glass. The residue was purified and gave gray crystals of  $\text{PhNC(PhICl)}_2$  from EtOH, which have the odor of anethole, m.  $56^\circ$ . The reaction involved appears to be  $3\text{PhICl}_2 + \text{PhNH}_2 \longrightarrow 2\text{HCl} + \text{PhNC(PhICl)}_2$ ; it will be studied further.

E. J. WITZEMANN

**Photo-bromination of toluene and xylene.** TORSTEN SWENSSON. *Z. wiss. Photochem.* 20, 206-18(1921).—The rate of absorption of Br by PhMe and xylene in the presence of benzene, alc.,  $\text{CCl}_4$ , or HBr, when exposed to light from a quartz Hg lamp at  $20^\circ$ , has been investigated. The results show that alc. has a negative catalytic action on the process owing to its removal of the HBr from the sphere of action. HBr catalyzes the reaction very strongly in the positive sense, and at the same time it is decompd.

J. C. S.

**Preparation of *p*-nitrotoluene *o*-sulfonic acid from cymene.** S. V. HINTIKKA. *Ann. Acad. Sci. Fennicae* [A] 10, 1-4(1917).—In the prepn. of nitrocymenesulfonic acid by the method of Errera (*Gazz. chim. ital.* 21, 65-76), cymene is treated successively with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  dild., and neutralized with  $\text{BaCO}_3$ . The mother liquor after the crystn. of the Ba salt of nitrocymene-*o*-sulfonic acid gives, with the required quantity of  $\text{H}_2\text{SO}_4$ , prisms of *p*-nitrotoluene-*o*-sulfonic acid,  $\text{SO}_3\text{H.C}_6\text{H}_4\text{Me.NO}_2$  aq., m.  $133.5^\circ$ . *p*-Aminotoluene-*o*-sulfonic acid,  $\text{SO}_3\text{H.C}_6\text{H}_4\text{Me.NH}_2\text{H}_2\text{O}$ , forms rhombohedrons, sol. in water. Nitrotoluenesulfonic acid gives, on boiling with NaOH and a suitable reducing agent, the well known stilbene colors. Diaminostilbenedisulfonic acid may also be obtained from it.

J. C. S.

**Reduction of emulsified nitro compounds. I.  $\beta$ -Phenylhydroxylamine from nitrobenzene.** ARTHUR LAPWORTH AND LEONORE KLETZ PEARSON. Univ. Manchester. *J. Chem. Soc.* 119, 765-8(1921).—The need for phenacetin during the war indicated the need of a simple method of manufg.  $\text{PhNHOH}$ . At first emulsions of  $\text{PhNO}_2$ ,  $\text{NH}_4\text{HS}$  and kieselguhr in  $\text{H}_2\text{O}$  were used, but later NaHS was used and the kieselguhr was replaced by  $\text{CaCl}_2$ , which causes the pptn. of finely divided  $\text{Ca(OH)}_2$  or "basic" sulfides, in the presence of which emulsification takes place readily. 72-74% yields of  $\text{PhNHOH}$  may be obtained as follows: 27.6 g.  $\text{NaS} \cdot 9\text{H}_2\text{O}$  in 21.8 cc.  $\text{H}_2\text{O}$  are cautiously treated through a funnel extending to the bottom of the cylinder, with 10.5 cc.  $\text{HCl}$  (d. 1.16). This soln. is placed in a stoppered flask with 5 g.  $\text{PhNO}_2$  and 5 g.  $\text{CaCl}_2$  in a little  $\text{H}_2\text{O}$ , the whole being at  $15^\circ$ . On shaking the mixt. emulsifies and the temp. should not exceed  $30^\circ$ . After about 0.75 hr., crystals begin to appear. After about 1.5 hrs. the oil has disappeared (critical stage), and at this stage 6 g.  $\text{NH}_4\text{Cl}$  are added, the whole is shaken, and on filtering, about 3.3 g. pure, cryst.  $\text{PhNHOH}$  are obtained. In working larger quantities, it might be better to operate with a smaller proportion of  $\text{H}_2\text{O}$  and to regulate the temp. by suitable additions of ice. II. Some extensions of the method. ROBERT DOWNS HAWORTH AND ARTHUR LAPWORTH. *Ibid* 768-77. —The emulsification process described above has been extended to the reduction of  $\alpha\text{-MeC}_6\text{H}_4\text{NO}_2$  and to a



number of  $\text{NO}_2$  compds. of the aromatic series which are solid at the ordinary temp.  $o\text{-MeC}_6\text{H}_4\text{NO}_2$  and  $o\text{-ClC}_6\text{H}_4\text{NO}_2$ , the former as such and the latter in  $\text{C}_6\text{H}_6$ , do not at once yield solid hydroxylamines, but give oils containing about 15 and 62%, resp., of the corresponding hydroxylamines. The process gives satisfactory results with  $p\text{-MeC}_6\text{H}_4\text{NO}_2$ ,  $p\text{-ClC}_6\text{H}_4\text{NO}_2$ ,  $p\text{-IC}_6\text{H}_4\text{NO}_2$ ,  $m\text{-ClC}_6\text{H}_4\text{NO}_2$ ,  $m\text{-BrC}_6\text{H}_4\text{NO}_2$ ,  $\alpha\text{-C}_{10}\text{H}_7\text{NO}_2$ , using solns. or suspensions of these compds. in  $\text{C}_6\text{H}_6$ , the  $\beta$ -substituted hydroxylamine being obtained at once in solid form and in yields usually exceeding, sometimes considerably, 50% of the theory, a few % only remaining in the filtrate. *o*-Chloronitrosobenzene, by oxidizing the oil containing the hydroxylamine, needles, m.  $56\text{--}7^\circ$ . *m*-Chlorophenylhydroxylamine, plates from  $\text{C}_6\text{H}_6$ , m.  $49^\circ$ . *m*-Chloronitrosobenzene, needles, m.  $72^\circ$ . Its solns. are green.  $\alpha\text{-C}_{10}\text{H}_7\text{NO}_2$  gives  $\text{C}_{10}\text{H}_7\text{NIOH}$  if  $\text{CaCl}_2$  is used but gives as high as 73%  $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$  when kieselguhr is used. Nitroanthraquinone gives rise to the hydroxylamine or  $\text{NH}_2$  compd., depending upon the concn. of the hydrosulfide soln. 73% yields of hydroxylamine were obtained as follows: 5 g.  $\text{NO}_2$  deriv. in 20 cc.  $\text{C}_6\text{H}_6$  were emulsified with 21 g. standard hydrosulfide soln. dild. to 75 cc. with the aid of 3 g.  $\text{CaCl}_2$ , stirred for 45 min., 3 g.  $\text{NH}_4\text{Cl}$  added and the solid filtered.  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  and  $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{Me}$  gave mainly the dinitroazoxy compds. *m*- and *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$  are reduced to the corresponding diamines. The reaction is not applicable to  $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH}$ , owing to the slight soly. of the Na salt. C. J. WESR

**Amines. IX.** The alkylation of aromatic amines by heating with aliphatic alcohols. ARTHUR J. HILL AND JOHN J. DONLEAVY. Yale Univ. *J. Ind. Eng. Chem.* **13**, 504-9 (1921).—A continuation of research in the action of catalysts upon the formation of  $\text{PhNEt}_2$  from  $\text{PhNH}_2\text{Cl}$  and  $\text{EtOH}$  (*C. A.* **14**, 2618). The reaction is applied to the action of: (1)  $\text{EtOH}$  on *o*-, *m*- and *p*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$  and (2)  $\text{BuOH}$  on  $\text{PhNH}_2\text{Cl}$ , *o*-, *m*- and *p*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$ . The object was to obtain the max. yield of tertiary base. Three predominant factors were found to influence its formation: (1) alc. concn.; (2) nature of the catalyst, and (3) temp. A large excess of alc. (10 mols.) decreases the formation of  $\text{PhNHR}$  (*C. A.* **14**, 2618). A mixt. of  $\text{CaCl}_2$ ,  $\text{NaBr}$  and  $\text{CuCl}_2$  increases the yield of  $\text{PhNR}$ ; (*C. A.* **14**, 177, 1816). Above  $175\text{--}80^\circ$ , however, they tend to form  $p\text{-RC}_6\text{H}_4\text{NHR}$ . The usual inactivity of *o*- compared with *m*- and *p*-compds. is found in this new investigation. *p*- and *m*- $\text{MeC}_6\text{H}_4\text{NH}_2$  were ethylated or butylated to the same extent, but *o*- $\text{MeC}_6\text{H}_4\text{NH}_2$  14-16% less with  $\text{EtOH}$  and 29-31% less with  $\text{BuOH}$  (cf. *Ber.* **5**, 707(1872); **8**, 61(1875); **18**, 1824(1885); **32**, 1401(1899); **33**, 345, 1967(1900); *J. prakt. Chem.* **65**, 252(1902); *Ann.* **346**, 128(1906), and *C. A.* **13**, 711).  $\text{BuOH}$  was of less activity than  $\text{EtOH}$ , but was relatively much more affected by catalysts. The reactions were carried out in an autoclave, the alc. was removed by distn. at low pressure, the residue made alk. with  $\text{NaOH}$ , and the bases steam distd. Those from  $\text{BuOH}$  were extd. directly with  $\text{Et}_2\text{O}$ . They were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The formation of *o*-, *m*- and *p*- $\text{MeC}_6\text{H}_4\text{NEt}_2$  has been recorded previously (*Ber.* **16**, 29(1883); **25**, 1613(1892); **35**, 3540(1902); *Ann.* **93**, 313(1855); *Am. Chem. J.* **7**, 119(1885)). *o*- and *m*- $\text{MeC}_6\text{H}_4\text{NBu}_2$  have not been prepd. previously. Maximum yields were obtained in all cases at  $175\text{--}80^\circ$  as follows: (1) *p*- $\text{MeC}_6\text{H}_4\text{NEt}_2$  92.1% by heating 100 g. *p*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$  and 320 g.  $\text{EtOH}$  for 8 hrs. with 10 g.  $\text{NaBr}$  and 5 g. powdered  $\text{Cu}$ ; (2) *m*- $\text{MeC}_6\text{H}_4\text{NEt}_2$  90.25% from 50 g. *m*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$  and 160 g.  $\text{EtOH}$  for 8 hrs. with 5 g.  $\text{NaBr}$ , 5 g.  $\text{CaCl}_2$  and 2.5 g.  $\text{CuCl}_2$ ; (3) *o*- $\text{MeC}_6\text{H}_4\text{NEt}_2$  from 100 g. *o*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$  and 320 g.  $\text{EtOH}$  for 8 hrs. with 10 g.  $\text{NaBr}$ , 10 g.  $\text{CaCl}_2$  and 5 g.  $\text{CuCl}_2$ ; (4)  $\text{PhNBu}_2$  75% from 50 g.  $\text{PhNH}_2\text{Cl}$  and 285 g.  $\text{BuOH}$  for 8 hrs. with 5 g.  $\text{NaBr}$ , 5 g.  $\text{CaCl}_2$  and 2.5 g.  $\text{CuCl}_2$  (*C. A.* **12**, 682); (5) *p*- $\text{MeC}_6\text{H}_4\text{NBu}_2$  77.5% from 50 g. *p*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$  and 255 g.  $\text{BuOH}$  for 12 hrs. with 5 g.  $\text{NaBr}$ , 5 g.  $\text{CaCl}_2$  and 2.5 g.  $\text{CuCl}_2$ . It had to be isolated by Hinsberg's method (*Ber.* **23**, 2962(1890)); (6) *m*- $\text{MeC}_6\text{H}_4\text{NBu}_2$  79.8% from 50 g. *m*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{Cl}$  and 255 g.  $\text{BuOH}$  for 8



hrs. with 5 g. NaBr, 5 g. CaCl<sub>2</sub> and 2.5 g. CuCl<sub>2</sub>, isolated by Hinsberg's method, was a pale yellow oil, *b*<sub>715</sub> 278-80°; (7) *o*-MeC<sub>6</sub>H<sub>4</sub>NBu<sub>3</sub> 48.5% from 50 g. *o*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>Cl and 255 g. BuOH for 8 hrs. with 5 g. NaBr, 5 g. CaCl<sub>2</sub> and 2.5 g. CuCl<sub>2</sub>, isolated by Hinsberg's method, was an oil, *b*<sub>715</sub> 256-8°. C. C. DAVIS

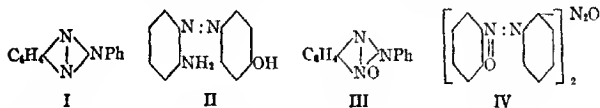
**Partial reduction of nitroazoxybenzenes with hydrogen and platinum.** G. CUSMANO AND L. DELLA NAVE. R. Ist. Studi Sup., Florence. *Gazz. chim. ital.* 51, 1, 65-70(1921).—The few existing data on the reduction of nitroazoxy compds. show that with such reagents as (NH<sub>4</sub>)<sub>2</sub>S and Sn + HCl the azoxy group—N:N(O)—is more rapidly reduced than the NO<sub>2</sub> group. In a preceding paper (C. A. 14, 1314) C. showed that with Pt black and H<sub>2</sub> an equimol. mixt. of Ph<sub>2</sub>N<sub>2</sub>O and *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Me gave *p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Me, while the Ph<sub>2</sub>N<sub>2</sub>O remained unchanged. Moreover (3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>N<sub>2</sub>O treated in this way gave 3,3'-azoxyaniline. Moreover the NHOH group is more rapidly reduced than NO<sub>2</sub> contrary to what occurs with other processes. C. and N. have studied the reduction of *o*-nitroazoxybenzene (A). With (NH<sub>4</sub>)<sub>2</sub>S (Zinin, *Ann.* 114, 222(1861)) A gives azonitrosobenzene; with Sn + HCl (Werner, *Stiasny, Ber.* 32, 3271(1890)) A gives phenylazidobenzene. When, however, an Et<sub>2</sub>O soln. of A, with Pt black present, is agitated with 2 mols. H<sub>2</sub> *o*-hydroxylaminoazobenzene, *o*-aminoazoxybenzene (B), *o*-nitroazobenzene (C), *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (D) and PhNH<sub>2</sub> (E) were obtained besides unchanged A. If 3 mols. H<sub>2</sub> were used B, D, and E and nitrosoazobenzene were obtained. The reduction proceeds in 2 directions (1) the NO<sub>2</sub> group is attacked while the oxyazo is spared, giving the NHOH and NH<sub>2</sub> groups; (2) the azoxy group is attacked. *o*-Hydroxylamino- and *o*-aminoazoxybenzene were not obtained. A .05 l. bottle fitted with a ground-glass stopper supplied with a cock through which the Et<sub>2</sub>O soln. of 3-4 g. A was introduced together with several cc. Pt black was used. The air was then removed by suction and H<sub>2</sub> admitted, the bottle was placed upon an agitator and the H<sub>2</sub> replenished from time to time by opening the cock until 2 mols. had been absorbed. The absorption required about 0.5 hr. The Pt was filtered off. The soln., which was bright yellow at the beginning, was now deep orange in color. On evap. on the H<sub>2</sub>O bath yellow crystals of *o*-hydroxylaminoazobenzene (F) mixed with red crystals of C were obtained. F was purified by digestion with Et<sub>2</sub>O which readily dissolves C. F was easily purified and gave bright yellow crystals that soften 115° and m. 118°. With F PhNCO combines easily on mixing to give an addition product as flat bright yellow crystals, m. 140° (decompn.). F reduced with 1 mol. H<sub>2</sub> (Pt) gave mostly B and some D. F readily undergoes oxidation. With HgO for 10 mins. on the H<sub>2</sub>O bath it gave *o*-nitrosoazoxybenzene as S-yellow crystals, m. 106°. C was recovered from the Et<sub>2</sub>O solns obtained with F and seps. as blood-red crystals, m. 105-6°, not identical with the *o*-nitroazobenzene obtained by Janovsky (*Monatsh.* 7, 129(1887)), which m. 127°. C reduced with 1 mol. H<sub>2</sub> gave azonitrosobenzene, like the nitro-nitrosobenzene of Bamberger and Hübner (*Ber.* 36, 3818(1903)) but is not identical with their product. The mother liquors from F and C gave a yellow-orange oil which refused to cryst. and was taken up in Et<sub>2</sub>O and treated with a little dil. HCl several times in order to remove D. Upon adding concd. HCl B was pptd. The Et<sub>2</sub>O contained a little unchanged A. Dil. alkali pptd. B which was recrystd. from EtOH, prisms, m. about 98°; the salts with HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are colorless and well crystd. B combines in the cold with Ac<sub>2</sub>O, giving *acetyl-o-aminoazoxybenzene*, bright yellow needles, m. 56°. The reduction of A with 3 mols. H<sub>2</sub> was carried out in the same way and gave the products mentioned above, which were sepd. by successive extr. of the bases from the Et<sub>2</sub>O soln. with HCl and the crystn. of the azonitrosobenzene from the Et<sub>2</sub>O soln. remaining after the extrn.

E. J. WITZEMANN

**Intramolecular condensation by means of the —N:N(O)— group of the azoxy com-**



pounds. G. CUSMANO. *Gazz. chim. ital.* 51, II, 71-4(1921); *Atti accad. Lincei* 29, II, 365-8.—The expts. described in the preceding abst. gave C. an opportunity to observe an intramol. condensation of the  $-N:N(O)-$  group in azoxy compds. and illustrates the oxidizing property of this group. *o*-Aminoazoxybenzene (A) heated in concd.  $H_2SO_4$  under the same conditions in which the azoxy compds. change into hydroxyazo compds. eliminates 1 mol.  $H_2O$  between the 2 N groups, giving phenylazimidobenzene (I). This reaction parallels the well known action of  $CrO_3$  on *o*-



aminoazotoluene in which by oxidizing off the 2 H atoms of the  $NH_2$  group the homolog of I is obtained. At the same time that about 90% I is formed from A a portion undergoes the Wallach transposition, giving *o*-amino *p*'-hydroxyazobenzene (II). Protecting the  $NH_2$  group of A with Ac causes a higher yield of II. In *o*-hydroxylaminoazoxybenzene (B)  $H_2O$  is eliminated by allowing a trace of NaOH to react in the EtOH soln., giving the phenylazimidobenzene oxide (III) (so-called azonitrosobenzene). This is the method used by Werner and Stiasny (*Ber.* 32, 3267) for obtaining nitrosozonitrosobenzene from *o*,*p*-dinitrohydrazobenzene. In these 2 new intramol. condensations the  $-N:N(O)-$  group acts upon  $NH_2$  or upon  $-N(O)N_2$  as the  $NO_2$  group acts upon the hydrazoic group  $-NH.NH-$ . Under the conditions described B is also transformed in part into a triazoxybenzene (IV). A in concd.  $H_2SO_4$  was heated in a  $H_2O$  bath for 1 hr. and was then poured into much  $H_2O$  by which I was pptd.; long colorless crystals from EtOH, m.  $105^\circ$ . The acid soln. was alkalinized with  $Na_2CO_3$  to sep. I and then II was pptd. with EtOH: yellow crystals, m.  $159^\circ$ . The Na salt of II is yellow and easily sol. in  $H_2O$  while the K salt is blood-red. With 11% HCl II gives a little sol. green salt and with more concd. acid it gives a red salt. II combines with  $Ac_2O$ . In order to det. its constitution II was dissolved in dry Et<sub>2</sub>O and reduced with  $H_2$  in the presence of Pt black and gave *p*- $H_2NC_6H_4OH$  and *o*- $C_6H_4(NH_2)_2$ . An EtOH soln. of 1.47 g. B treated with a few drops of NaOH gave 0.82 g. IV and 0.24 g. III and a small amt. of another red substance. E. J. WITZEMANN

**Dinitrotolylhydrazines.** OSCAR LISLE BRAOY AND JOHN HERBERT BOWMAN. Univ. College. *J. Chem. Soc.* 119, 894-900(1921).—The action of  $N_2H_4.H_2O$  on the various  $MeC_6H_2(NO_2)_3$  gives the corresponding dinitrotolylhydrazines. 2,4-Dinitro-*m*-tolylhydrazine, from 11 g. 2,3,4-( $NO_2$ )<sub>3</sub> $C_6H_2Me$  in 150 cc. boiling alc. and 10 cc.  $N_2H_4.H_2O$  (50%) in 20 cc. alc., with cooling, long red prismatic needles from alc. or  $C_6H_6$ , m.  $170^\circ$ . Acetate, long, brilliant yellow rhombic needles, m.  $193^\circ$  (decompn.). Heated 30 min. with AcOH and  $Cu(OAc)_2$ , 2,4-( $O_2N$ )<sub>2</sub> $C_6H_2Me$  is formed. 3-Chloro-2,4-dinitrotoluene, long silky, pale yellow needles, m.  $92^\circ$ , by the action of  $CuCl_2$  on the hydrazine. 3-Iodo-2,4-dinitrotoluene, by the action of I in alc. on the hydrazine, yellow leaflets, m.  $117^\circ$ . When boiled with  $N_2H_4.H_2O$  the hydrazine forms 4-nitro-1-hydroxy-5(7)-methyl-1,2,3-benzotriazole,  $C_7H_5O_2N_4.H_2O$ , pale yellow, hexagonal prisms with 1 mol.  $H_2O$ , m. (anhydrous)  $205^\circ$ . The soln. in alkalis or carbonates is deep orange-red. Heated rapidly, it deflagrates and in a closed tube explodes violently. Hydrazine salt,  $C_7H_5O_2N_4.N_2H_4$ , orange needles. 2,4-Dinitro-*m*-tolylazoimide, silvery leaflets, m.  $89^\circ$ . 2,4-Dinitro-*m*-tolylhydrazones: formaldehyde by adding HCHO to the hydrazine, fine yellow needles, m.  $132^\circ$ ; acetaldehyde, yellow cryst. powder, m.  $112^\circ$ ; propionaldehyde, long orange-yellow tables, m.  $100^\circ$ ; butyraldehyde,  $C_4H_9O_2N_4$ , orange-red prisms, m.  $86^\circ$ ; benzaldehyde, orange-red needles, m.  $185^\circ$ ;



acetone, long orange-red needles, m. 102°; methyl ethyl ketone, orange-yellow needles, m. 94°. 3,5-Dinitro-*o*-tolylhydrazine, orange flaky needles, m. 169° (decompn.). Acetone derivative, scarlet needles, m. 128°. Benzaldehyde derivative, vermilion powder, m. 194°. 3,5-Dinitro-*p*-tolylhydrazine, from 3,4,5-(O<sub>2</sub>N)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>Me, lustrous, Cu-colored plates, m. 139°. Benzaldehyde derivative, scarlet leaflets, m. 214°. 4-Nitro-1-hydroxy-6-methyl-1,2,3-benzotriazole, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N<sub>4</sub>, pale yellow, silky needles, did not m. 230°.

C. J. West

**Cyanonitrophenylhydrazines.** W. BORSCHÉ. Univ. Göttingen. *Ber.* **54B**, 660-9 (1921); cf. *C. A.* **11**, 959.—4,3-Br(O<sub>2</sub>N)C<sub>6</sub>H<sub>2</sub>CN (11.35 g.) in 120 cc. hot alc. treated with 6.6 g. com. (90°C) N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and 15 cc. alc. yields almost quant. 4-cyano-2-nitrophenylhydrazine (A), fine needles from alc., m. 221° (foaming), not visibly changed by cold NaOH, but 1.5 g. gently warmed with 25 cc. of *N* NaOH dissolves and with dil. HCl gives 6-cyanobenzazimidol, NCC<sub>6</sub>H<sub>3</sub>N:N.NOH, needles from EtOH-H<sub>2</sub>O, turns brown

210°, deflagrates 218-9°. A smoothly dissolves in hot HCl and on cooling seps. as the hydrochloride in fine orange-red needles; small amts. dissolve without any striking phenomena in concd. H<sub>2</sub>SO<sub>4</sub> but larger amts. decomp. explosively. Attempts to convert it into ethyl 3-nitro-4-hydrazinobenzoate by warming it with alc. H<sub>2</sub>SO<sub>4</sub> led only to the formation of a viscous red-brown resin; the ester, crystals from EtOH-H<sub>2</sub>O, m. 103°, is easily obtained, however, from 2.74 g. 4,2-Br(O<sub>2</sub>N)C<sub>6</sub>H<sub>2</sub>CO<sub>2</sub>Et in 20 cc. alc. heated several hrs. with 1.1 g. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O. 3-Nitro-4-acetylhydrazinobenzonitrile, from A boiled several hrs. with 15 parts AcOH, and pptd. with 5 vols. H<sub>2</sub>O, yellow needles from dil. alc., m. 203°; with a mixt. of 2 parts AcOH with 1 part Ac<sub>2</sub>O, there is obtained, even at H<sub>2</sub>O bath temp., the 4-diacylhydrazinobenzonitrile compound, yellow leaflets from 33% AcOH, m. 185°, sol. without change in NaOH with deep violet-red color. 4-Benzoylhydrazinobenzonitrile, from A and BzCl in boiling C<sub>6</sub>H<sub>5</sub>N or from Br(O<sub>2</sub>N)C<sub>6</sub>H<sub>2</sub>CN heated several hrs. with BzNHNH<sub>2</sub> and NaOAc in alc., golden yellow leaves from alc., m. 226-7°; with 2 mols. BzCl is obtained the 4-dibenzoylhydrazinobenzonitrile compound, bright yellow crystals from alc., m. 173-4°, sol. in NaOH with violet-red color. Anisaldehyde 4-cyano-2-nitrophenylhydrazine, from 0.5 g. A in 125 cc. of 0.1 *N* HCl and 0.5 g. MeOC<sub>6</sub>H<sub>4</sub>CHO in 25 cc. alc., fine blood-red needles from AcOH, m. 239°, sol. in alc. NaOH with deep violet color. Acetone 4-cyano-2-nitrophenylhydrazine, from 0.6 g. A in 180 cc. of 0.1 *N* HCl and a few cc. of Me<sub>2</sub>CO, flat orange-yellow needles from alc., m. 128-9°, sol. in alc. NaOH with red-violet color. Benzophenone 4-cyano-2-nitrophenylhydrazine, from 0.6 g. A in 90 cc. 0.2 *N* HCl + 90 cc. alc. and 0.6 g. Ph<sub>2</sub>CO heated 4 hrs. on the H<sub>2</sub>O bath, bright red cryst. powder, m. 208-9°, sol. only with difficulty even in hot alc. NaOH with dirty red-brown color. 4'-Cyano-2'-nitrobenzenazo-4-phenol, from 0.9 g. A in 300 cc. of hot 0.1 *N* HCl and 0.54 g. quinone in 10 cc. alc., flat dark brown needles from EtOH-H<sub>2</sub>O, m. 236-7°, sol. in NaOH with yellowish red color. Quinone oxime 4-cyano-2-nitrophenylhydrazine, from 1.8 g. A in 180 cc. alc. + 4 cc. fuming HCl and 1.2 g. quinone oxime in 20 cc. alc., dark red crystals, m. 229° (decompn.), sol. in dil. NaOH with dark red color; yield, almost quant.; 1.5 g. boiled up with 48 cc. AcOH + 2 cc. HNO<sub>3</sub> (d. 1.39) gives 4'-cyano-2',4-dinitrobenzene, light brown microneedles from AcOH, m. 188-9°, becomes extraordinarily electrified on rubbing. 3-Nitro-6-chlorobenzonitrile (6.3 g., from 5 g. *o*-ClC<sub>6</sub>H<sub>4</sub>CN allowed to stand 3-4 days in a closed vessel with 25 cc. HNO<sub>3</sub> (d. 1.52) and then poured into 250 cc. ice H<sub>2</sub>O), needles from alc., m. 108-9°; heated 4 hrs. on the H<sub>2</sub>O bath in alc. with 2 mols. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, it gives 2-cyano-4-nitrophenylhydrazine (B), fine red needles from PhNO<sub>2</sub>, m. 250°; 0.7 g. of this, boiled 5 hrs. with 16 cc. AcOH, yields acetic 2-cyano-4-nitrophenylhydrazide, yellow leaflets from AcOH, m. 308°, easily sol. with red color in dil. NaOH. B does not perceptibly react with BzNHNH<sub>2</sub> and NaOAc after 8 hrs. on the H<sub>2</sub>O bath but the ben-



*zoyl-2-cyano-4-nitrophenylhydrazine*, yellow needles, m. 223°, is obtained by benzoylating **B** in  $C_6H_5N$  and crystg. the product from  $Me_2CO-EtOH$ ; the first crop of crystals consists of the *dibenzoyl compound*, yellowish white spherical granules, m. 232–3°. *o-Hydroxybenzal-2-cyano-4-nitrophenylhydrazine*, from equimol. amts. of **B** and  $o-HOC_6H_4CHO$  heated a short time in aq. alc. on the  $H_2O$  bath, brownish yellow crystals from alc., m. 231°. *Anisal analog*, from 0.9 g.  $MeOC_6H_4CHO$  in 16 cc. alc. and 1.2 g. **B** in 24 cc.  $N HCl$  allowed to stand some time, yellow flocks of fine needles from very dil. alc. containing  $NaOAc$ , m. 163–5°. **B** could not be made to condense with  $Me_2CO$  and  $BzMe$  under the most varied conditions and with quinone and its oxime it also did not behave like **A**, giving, instead of the expected azo compds., only dark, finely flocculent, amorphous ppts. containing  $HCl$ . *5-Methyl-2-cyano-4-nitrophenylhydrazine (C)*, obtained almost quant. from 12 g. 4,6,3-MeBr( $O_2N$ ) $C_6H_3CN$  in 120 cc. alc. and 5.4 g.  $N_2H_4 \cdot H_2O$  heated 1 day on the  $H_2O$  bath, freed from most of the alc., boiled up with 300 cc. of 0.5  $N HCl$  and liberated from the resulting *hydrochloride* (stout orange-red needles) with  $Na_2CO_3$  or  $NaOAc$ , thick yellow-red prisms from abs. alc., m. 217–8°, dark red needles with 0.5  $H_2O$  from dil alc., changing at 185° into the anhydrous form, smoothly dissolves in  $NaOH$  with dark red color, the hot satd. soln. on cooling depositing crystals of the *sodium derivative*, which with  $AcOH$  regenerates **C**. The *acetyl derivative*, yellow leaflets from  $AcOH$ , m. 291–2°. Attempts to convert **C** into a hydrazobenzene deriv. by boiling 12 hrs. in alc. with  $NaOAc$  failed but 3 g. in 120 cc. alc. boiled 3 hrs. with 3.6 g. 2,4,6- $(O_2N)_3C_6H_2Cl$  and 3 g. crystd.  $NaOAc$  yielded 2.8 g. *5-methyl-2-cyano-4,2',4',6'-tetranitrohydrazobenzene*, bright red crystals from  $AcOH$ , m. 258–9° (decompn.), sol. in  $NaOH$  with deep violet color. **C** forms hydrazones only with aldehydes and not smoothly, a part decomp. with loss of  $N_2H_4$  so that the hydrazones are always mixed with varying amts. of azines; the extent of this decompn., which has thus far not been observed with the non-methylated compds., seems to depend on the nature of the  $C:O$  compd., for heating with  $Ph_2CO$  gives only the ketazine but no hydrazone. Equal amts. of **C** and  $o-HOC_6H_4CHO$  (1.2 g. each) heated 3 hrs. on the  $H_2O$  bath in 60 cc. alc. and allowed to stand overnight yield a mixt. of yellow needles and granules sepd. by fractionation from alc. into *o-hydroxybenzalazine*, m. 216°, and *o-hydroxybenzal-5-methyl-2-cyano-4-nitrophenylhydrazine*, light yellow needles from alc., m. 217–8°. Anisaldehyde (1.2 g.) under the same conditions gave 0.6 g. of the azine, yellowish needles from alc., m. turbid 168°, clear 178°, and the *hydrazone*, dark yellow cryst. powder from 50% alc., m. 172–3°, easily sol. in  $NaOH$  with red-yellow color. Finally  $Ph_2CO$  after 5 hrs. heating gave on addition of  $H_2O$  a milky turbidity quickly changing into the fine yellowish needles, m. 169°, of  $(Ph_2C:N)_2$ . C. A. R.

**2,4-Dinitro-5-chlorophenylhydrazine and 2,4-dinitro-1,5-dihydrazinobenzene.** W. BORSCHKE. Univ. Göttingen. *Ber.* 54B, 639–81 (1921).—1,5,2,4- $C_6H_2Cl(NO_2)_2$  (11.9 g.) in 120 cc. boiling alc. treated with 5.5 g.  $N_2H_4 \cdot H_2O$  in 20 cc. alc. in small portions gives 8–9 g. *2,4-dinitro-5-chlorophenylhydrazine (A)*, red-yellow leaflets from 15 parts  $AcOH$  + 10 parts alc., m. 198°, sol. in hot dil.  $NaOH$  with dark brown color and vigorous evolution of gas, the soln. soon becoming turbid and depositing brown viscous droplets on standing; **A** dissolves with difficulty in hot dil.  $HCl$  and on cooling seps. as the *hydrochloride* in fine yellow needles. *Acetyl derivative*, from **A** boiled 2 hrs. with 10 parts  $AcOH$ , fine yellow needles from alc., m. 192–3°, sol. in dil.  $NaOH$  with deep red-brown color and repptd. unchanged by acids; with a mixt. of equal parts  $AcOH$  and  $Ac_2O$  instead of  $Ac_2O$  there is obtained on the  $H_2O$  bath the *diacetyl derivative*, fine yellow needles from dil. alc., m. 131–2°. *2,4-Dinitro-4'-hydroxy-5-chlorozobenzene (B)*, from 4.7 g. **A** and 5 cc. fuming  $HCl$  in 200 cc. hot alc. treated with 2.2 g. quinone in 25 cc. alc., freed from 0.5 of the alc. after 1 hr. by distn. and dild. to incipient turbidity, brown



needles, m. 190–1°, sol. in dil. NaOH with bright violet-red color. *Quinone oxime 2,4-dinitro-5-chlorophenylhydrazone*, obtained almost quant. from the components in hot alc. HCl, dark red needles with steel-blue luster, decomp. 224–5°; 1.69 g. boiled a short time with 23 cc. AcOH and 2 cc. HNO<sub>3</sub> (d. 1.39) gives 1.2 g. *2,4,4'-trinitro-5-chloroazobenzene*, light red-brown powder from AcOH-H<sub>2</sub>O, m. 154°. *2,4-Dinitro-5-hydrazinoaniline* (3.1 g. from 3.3 g. 5,2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> in 50 cc. alc. heated 0.5 hr. on the H<sub>2</sub>O bath with the calcd. amt. of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), red-brown needles from PhNO<sub>2</sub>, m. 236–7° (decompn.), sol. in dil. NaOH with dark red color, difficultly sol. in boiling dil. HCl, sepg. on cooling as the *hydrochloride* in dark red needles; 1.07 g., finely powdered, boiled up with 200 cc. alc. + 40 cc. N HCl, filtered hot and treated with 0.24 g. quinone in 10 cc. alc. gives *2,4-dinitro-5-amino-1'-hydroxyazobenzene*, red-brown powder from dil. alc., decomp. about 140°, sol. in NaOH with orange-red color. *2,4-Dinitro-5-hydrazino-N-dimethylaniline*, obtained almost quant. from 2.45 g. 5,2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NMe<sub>2</sub> and 1.1 g. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in 75 cc. alc. heated 0.5 hr. on the H<sub>2</sub>O bath, bright red flat needles, m. 177–8°, quite easily sol. in dil. HCl; 0.6 g. in 30 cc. warm alc. + 1 cc. fuming HCl with 0.27 g. quinone in alc. gives *2,4-dinitro-5-dimethylamino-1'-hydroxyazobenzene*, red-brown needles from EtOH-H<sub>2</sub>O, m. 216–7°, sol. in NaOH with orange-red color. *Quinone oxime 2,4-dinitro-5-dimethylaminophenylhydrazone* (3.1 g. from 2.41 g. of the hydrazine in 120 cc. alc. + 4 cc. fuming HCl and 1.23 g. quinone oxime in 25 cc. alc.), heavy red-brown cryst. meal, m. 227°, sol. in NaOH with violet-red color; 1.2 g. boiled up with 50 cc. AcOH + 2.5 cc. HNO<sub>3</sub> (d. 1.39) yields *2,4,4'-trinitro-5-dimethylaminoozobenzene*, bright orange-red powder from AcOH, sinters 190°, m. 214–6°. *2,4-Dinitro-5-hydrazinodiphenylamine*, from 0.9 g. 5,2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHPh and 0.35 g. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O heated 2 hrs. in 90 cc. alc., fine orange-red needles, m. 197–8°, slowly decompd. with gas evolution by hot NaOH. *2,4-Dinitro-5-hydrazinophenol*, from 4.36 g. 5,2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(OH) in 50 cc. alc. heated 6 hrs. on the H<sub>2</sub>O bath with 3.3 g. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, cooled, filtered, extd. with 200 cc. boiling H<sub>2</sub>O and cautiously pptd. with dil. HNO<sub>3</sub> at room temp., fine egg-yellow flocks resembling yellow HgO when dry (yield, about 4 g.), sol. in about 200 parts hot alc. and sepg. in red-brown spherical granules, m. 197° (decompn.), sol. in warm aq. alc. HCl and in dil. NaOH but at once decompd. with vigorous foaming by the latter; boiled 2 hrs. with 20 parts AcOH it yields the *5-acetylhydrazino compound*, light yellow needles from 20 parts AcOH, m. 225–6° (decompn.). *Acetophenone 2,4-dinitro-5-hydroxyphenylhydrazone*, from 0.8 g. of the hydrazine in 50 cc. alc. + 50 cc. 0.5 N HCl treated hot with 0.5 g. BzMe in alc., fine brown needles from AcOH, m. 205–6°. *2,4-Dinitro-5,1'-dihydroxyazobenzene (C)*, from 1.07 g. of the hydrazine in 100 cc. of hot 50% alc. + 2.5 cc. fuming HCl and the calcd. amt. of alc. quinone, red-brown needles from EtOH-H<sub>2</sub>O, m. 218° (decompn.), sol. in NaOH with intense orange-red color; attempts to prep. it by treating 1.5 g. B 45 min. at 170° with 1.5 g. NaOAc and 6 g. AcNH<sub>2</sub> failed; a large part of the material decompd. and the rest yielded the *dibenzate* of C, which, when prepd. pure by benzoylating C in C<sub>6</sub>H<sub>5</sub>N, seps. from Me<sub>2</sub>CO (or AcOEt) + EtOH in fine needles, m. 166°. *Quinone oxime 2,4-dinitro-5-hydroxyphenylhydrazone* (1.3 g. from 1.07 g. of the hydrazine and 0.62 g. of the oxime), fine dark red cryst. meal, decomp. 213–5°, sol. in dil. NaOH with red-brown color; 1 g. boiled a few moments with 23 cc. AcOH and 2 cc. HNO<sub>3</sub> (d. 1.39) gives *2,4,4'-trinitro-5-hydroxyazobenzene*, red needles from 40 cc. AcOH + 10 cc. H<sub>2</sub>O, m. 179°. *Ethyl 2,4-dinitro-5-hydrazinophenylacetate* (2.4 g. from 2.76 g. 5,2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>Et in about 30 cc. hot alc. and 1.1 g. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), fine bright orange-red needles from alc., m. 174°, dissolves in hot dil. soda with a dark brown color which quickly fades and on addition of HNO<sub>3</sub> turns to yellow; after several days there sep. yellowish white granules changing after repeated crystn. from a little H<sub>2</sub>O into yellowish leaflets of *1-hydroxy-6-nitroazimidobenzene-5-acetic acid* (?), O<sub>2</sub>N(HO<sub>2</sub>CCCH<sub>2</sub>-



$C_6H_3N:N.NOH$ , darkens above  $200^\circ$ , deflagrates  $224^\circ$ . Diethyl 2,4-dinitro-5-hydrazino-

phenylmalonate (2.8 g. from 3.6 g.  $Cl(O_2N)_2C_6H_3CH(CO_2Et)_2$  and 1.1 g.  $N_2H_4.H_2O$  heated 1 hr. in 36 cc. alc.), blood-red prisms from alc., m.  $104-5^\circ$ , quite easily sol., but apparently not without change, in hot soda, only slightly in hot dil. HCl; 1 g. in 30 cc. alc. + 30 cc. *N* HCl with 0.3 g. quinone in alc. gives diethyl 2,4-dinitro-4'-hydroxyazobenzene-5-malonate, red needles from alc., m.  $138^\circ$ . Quinone oxime hydrazone, garnet-red rhombic leaflets with dark green surface reflex from 75 parts boiling alc., m.  $188^\circ$  (foaming), sol. in NaOH with deep violet color, oxidized by  $AcOH.HNO_3$ , but with considerable resinification, to the trinitroazobenzene. 4,6-Dinitro-1,3-dihydrazinobenzene (D) (9 g. from 9.6 g.  $C_6H_3Cl_2(NO_2)_2$  in 700 cc. hot alc. and an equal wt. of  $N_2H_4.H_2O$  in 50 cc. alc.), flat brown needles from  $PhNO_2$ , deflagrates  $246^\circ$  with deposition of soot, dissolves in hot NaOH with gas evolution, is only slightly sol. in aq. HCl, more so in aq. alc. HCl but is slowly changed on long boiling. Bis-*N*<sup>8</sup>-acetyl derivative, from 1 g. D boiled 2 hrs. under a reflux with 100 cc. AcOH, lemon-yellow needles, turn dark brown above  $280^\circ$ , sinter and m. completely about  $305^\circ$ . Formaldehyde 4,6-dinitrophenylene-1,3-dihydrazone,  $(O_2N)_2C_6H_3(NHN:CH_2)_2$ , from a hot filtered solu. of 1.14 g. D in 75 cc. alc. + 70 cc.  $H_2O$  + 5 cc. fuming HCl treated with a few cc. of com. 40% HCHO, then with 8 g. crystd. NaOAc and digested some hrs. on the  $H_2O$  bath, dark yellow microneedles from AcOH, brownish yellow flat needles from  $PhNO_2$ , turn brown on heating and m.  $247^\circ$  (decompn.). Benzaldehyde analog (?), obtained like the HCHO compd. or, more readily, by heating D in 30 parts  $PhNO_2$  1 hr. on the  $H_2O$  bath with the calcd. amt. of BzH, red, apparently homogeneous leaflets from  $PhNO_2$ , m.  $302-4^\circ$  (decompn.); the analytical results, however, do not agree well with the expected compn. or with any which can logically be deduced (found, C 58.35-58.55, H 3.94-4.07, N 18.31-18.70%). Acetone compound, pptd. from D in aq. alc. HCl by  $Me_2CO$  as a voluminous light yellow ppt., fine orange needles from AcOH or AcOEt, m.  $234-5^\circ$  (gas evolution). Ethyl acetoacetate compound, prepd. like the HCHO deriv., dark yellow leaves from alc., m.  $133-4^\circ$ . Benzophenone derivative, from 1.82 g.  $Ph_2CO$  in 36 cc. alc. heated on the  $H_2O$  bath 1 hr. with 1.14 g. D in 150 cc. aq. alc. HCl, treated with 8 g. crystd. NaOAc and heated 1 hr. longer, stout needles from  $PhNO_2$ , turns brown from about  $280^\circ$ , m.  $305^\circ$  (foaming). 4,6-Dinitro-1,3-bis-(4'-hydroxybenzenesazo)benzene dibenzoate, from 1.14 g. D in hot dil. alc. HCl and 1.08 g. quinone in 20 cc. alc. allowed to stand several days, evapd. spontaneously in a bowl, dried completely, taken up in 15 cc. warm  $C_3H_5N$ , treated with 1.4 g. BzCl, cooled, stirred up after some hrs. with an equal vol. of alc. and filtered, yellow-red powder, m.  $180-1^\circ$  (yield, about 1.4 g.); 1 g. in 20 cc. warm concd. HCl poured into 200 cc. AcOH yields a bright red, finely flocculent ppt. sol. in dil. NaOH with red-violet color and easily in hot alc.; on cautious addition of  $H_2O$ , there seps. on cooling the free hydroxy compound, microneedles, m.  $244-5^\circ$ . Quinone oxime 4,6-dinitrophenylene-1,3-dihydrazone, slowly seps. as a fine light red-brown powder when quinone oxime is substituted for quinone in the preceding expt.; it dissolves in dil. NaOH with reddish blue color and decomp.  $205^\circ$ ; no well defined substance has as yet been obtained by its oxidation with  $AcOH.HNO_3$ . Acetyl-4,6-dinitro-1,3-dihydrazinobenzene, from 2.74 g.  $Cl(O_2N)_2C_6H_3NHNHAc$  in 55 cc. hot alc. and 1.1 g.  $N_2H_4.H_2O$  in 5 cc. alc., yellow needles from alc., m.  $224^\circ$  (decompn.), sol. in NaOH or  $Na_2CO_3$  with deep red-brown color and evolves gas violently on gentle warming; 0.9 g. in 40 cc. hot alc. + 10 cc. *N* HCl with the calcd. amt. of BzMe gives the hydrazone  $AcNHNH(O_2N)_2C_6H_3NHN:CMePh$ , orange-red needles from AcOH, m.  $272^\circ$  (decompn.). 2,4-Dinitro-5-hydrazino-4'-hydroxyazobenzene, from 3.2 g. B in 65 cc. hot alc. heated 15 min. on the  $H_2O$  bath with 2 mols.  $N_2H_4.H_2O$ , red-brown crystals from  $PhNO_2$ , decomp.  $178-80^\circ$ ; 0.8 g.



boiled some time with 160 cc. alc. + 1 cc. fuming HCl, filtered hot and treated with 0.3 g. BzMe yields the *hydrazone*  $\text{HOC}_6\text{H}_4\text{N}:\text{N}(\text{O}_2\text{N})_2\text{C}_6\text{H}_2\text{NHN}$ : CMePh, dark red granules, m. 224°.

CHAS. A. ROULLER

**Organo-derivatives of bismuth. IV. Interaction of the halogen derivatives of tertiary aromatic bismuthines with organo derivatives of magnesium and mercury.** FREDERICK CHALLENGER AND CHARLES FREDERICK ALLPRESS. Univ. Manchester. *J. Chem. Soc.* 119, 913-26 (1921); cf. *C. A.* 14, 2781.—Because of the failure which has accompanied many attempts to prep. mixed aromatic bismuthines of the type  $\text{BiR}'\text{R}''$ , the action of the Grignard reagent has been studied.  $\alpha\text{-C}_{10}\text{H}_7\text{Ph}_2\text{Bi}$  and  $\text{ICl}$  gave  $\text{Ph}_2\text{BiCl}$ .  $(p\text{-MeC}_6\text{H}_4)_3\text{Bi}$  and  $\text{BiCl}_3$  in dry  $\text{Et}_2\text{O}$  gave *di-p-tolylchlorobismuthine*,  $\text{C}_6\text{H}_4\text{ClBi}$ , sol. in  $\text{CHCl}_3$ , needles, m. 181°, and *p-tolylchlorobismuthine*,  $\text{C}_6\text{H}_4\text{Cl}_2\text{Bi}$ , insol. in  $\text{CHCl}_3$ , yellow needles, m. 206-7°. The action of Na upon  $\text{Ph}_2\text{BiBr}$  and  $\alpha\text{-C}_{10}\text{H}_7\text{Br}$  gave  $\text{Ph}_3\text{Bi}$ , as did Cu bronze.  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$  and  $\text{BiCl}_3$  gave *di- $\alpha$ -naphthylchlorobismuthine*,  $\text{C}_{10}\text{H}_7\text{ClBi}$ , fine yellow needles, m. 168°. It is very susceptible to moisture. When 1 mol.  $\text{BiBr}_3$  reacts upon 2 mols.  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$ ,  *$\alpha$ -naphthylhydibromobismuthine*, deep orange solid, m. 208°, results. 1.2 mols.  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  and 1.7 g.  $(p\text{-MeC}_6\text{H}_4)_3\text{BiCl}$  gave only  $(p\text{-MeC}_6\text{H}_4)_3\text{Bi}$ .  $(\alpha\text{-C}_{10}\text{H}_7)_2\text{BiCl}$  gave  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$ . 1,3,4- $\text{Me}_3\text{C}_6\text{H}_3\text{MgI}$  with  $\text{Ph}_2\text{BiCl}$  gave  $\text{Ph}_3\text{Bi}$  and with  $(p\text{-MeC}_6\text{H}_4)_3\text{BiCl}$  gave  $(p\text{-MeC}_6\text{H}_4)_3\text{Bi}$ .  $\text{PhMgBr}$  and  $\alpha\text{-C}_{10}\text{H}_7\text{BiBr}_2$  gave  $\text{Ph}_3\text{Bi}$  and  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$ . When the mixt. was allowed to stand at room temp. for 2 weeks about equal amts. of  $\text{Ph}_3\text{Bi}$  and  $\text{Ph}_2(\alpha\text{-C}_{10}\text{H}_7)_2\text{Bi}$  were formed. With  $p\text{-MeC}_6\text{H}_4\text{MgBr}$ ,  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$  was isolated.  $\text{Ph}_2\text{BiBr}$  and  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  gave  $\text{Ph}_3\text{Bi}$ ,  $\text{BiOBr}_2$  and some  $\text{Ph}_2\text{BiBr}$ .  $\text{PhMgBr}$  and  $(\alpha\text{-C}_{10}\text{H}_7)_2\text{BiBr}$  gave  $\text{PhBr}$ , traces of  $\text{Ph}_2$  and  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$ .  $\text{MeMgI}$  and  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{BiBr}_2$  gave  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$ .  $\text{HgPh}_2$  and  $\text{BiBr}_3$  in dry  $\text{Et}_2\text{O}$  gave  $\text{Ph}_3\text{Bi}$ .  $\text{HgPh}_2$  and  $\alpha\text{-C}_{10}\text{H}_7\text{BiBr}_2$  gave  $\text{HgPhBr}$ ,  $\text{Ph}_3\text{Bi}$  and  $\text{Hg}(\alpha\text{-C}_{10}\text{H}_7)_2$ .  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{BiBr}_2$  does not react with  $\text{HgPh}_2$  at room temp. In boiling  $\text{C}_6\text{H}_6$ ,  $\text{PhBr}$ ,  $\text{PhHgBr}$  and  $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}$  are formed, together with smaller amts. of  $\text{Ph}_3\text{Bi}$  and  $(\alpha\text{-C}_{10}\text{H}_7)_2\text{Hg}$ .  $\text{MeMgI}$  and  $\text{Ph}_3\text{AsCl}_2$  gave  $\text{Ph}_3\text{As}$  and  $\text{Ph}_3\text{As}(\text{OH})_2$ .  $\text{PhMgBr}$  behaved similarly.  $\text{MeMgI}$  and  $\text{Ph}_3\text{SbCl}_2$  gave  $\text{Ph}_3\text{Sb}$  and possibly a stibonium deriv.  $\text{BiCl}_3$  combines with  $\text{PhN}_2\text{Cl}$  to form a stable additive product which is being examd.

C. J. WEST

**Organic derivatives of silicon. XXV. Saturated and unsaturated silicohydrocarbons,  $\text{Si}_4\text{Ph}_8$ .** FREDERICK STANLEY KIPPING AND JAMES EDWIN SANDS. Univ. Coll. *J. Chem. Soc.* 119, 830-47 (1921); cf. *C. A.* 15, 2116.—The action of Na upon  $\text{Ph}_3\text{SiCl}$  gives a complex mixt., from which so far 3 cryst. compds. have been isolated. Two of these appear to be  $\text{Si}_4\text{Ph}_8$ , although no formulas are suggested to account for the isomerism. The  $\text{Ph}_3\text{SiCl}$  is dild. with 3-10 vols.  $\text{C}_2\text{H}_4$  or  $\text{C}_2\text{H}_{10}$  and heated with Na for 15 min. After cooling and filtering, the dark blue residue is extd. with  $\text{C}_2\text{H}_6$ , from which the "unsaturated" silicohydrocarbon,  $\text{Si}_4\text{Ph}_8$ , seps. and crystals from  $\text{C}_2\text{H}_6$  in short, flat prisms, m. about 335°. Heated on a watch glass, they decrepitate violently. It is almost insol. in most of the org. solvents at room temp., but is appreciably sol. in  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$ . 100 g.  $\text{C}_2\text{H}_6$  dissolve approx. 0.21 g. at 15.5° and 1.72 g. at 80°. It is sol. in boiling  $\text{PhNH}_2$ ,  $\text{PhCH}_2\text{OH}$  and  $\text{PhOH}$  but undergoes some decomp. on boiling. It reacts readily with I, in soln. or suspension in  $\text{C}_6\text{H}_6$ , giving *octaphenylsilole*, *silicotetralene*,  $\text{Si}_4\text{Ph}_8\text{I}_2$ , highly lustrous, very acute rhomboidal plates, which do not change at 250°. The reaction is of such a character that the hydrocarbon can be titrated with I. Upon hydrolysis with  $\text{NH}_4\text{OH}$  in  $\text{Me}_2\text{CO}$ , at least 4 products were obtained. The main product of the hydrolysis was *octaphenylsilicotetralene oxide*,  $\text{Si}_4\text{Ph}_8\text{O}$ , micro-needles from  $\text{CHCl}_3\text{-Me}_2\text{CO}$  or  $\text{C}_6\text{H}_6\text{-Me}_2\text{CO}$ , or lustrous rosetts of long transparent prisms from  $\text{PhNH}_2$ ,  $\text{PhNO}_2$  or  $\text{AcCH}_3\text{CO}_2\text{Et}$ , which m. 210-245°, depending on the manner of heating. About 15% was a glue-like substance sol. in cold  $\text{Me}_2\text{CO}$ . The other 2 products are discussed below. The action of  $\text{C}_2\text{H}_5\text{Cl}_4$  decomps. the hydrocarbon,



giving a small amt. of a *dichloride* (?),  $\text{Si}_4\text{Ph}_8\text{Cl}_2$ , m. about  $180^\circ$ , and upon addition of  $\text{H}_2\text{O}$  to the filtrate a ppt. resembling that obtained on hydrolysis of the iodide. The action of boiling  $\text{PhNO}_2$  on the hydrocarbon gives, as the principal product, an *oxide*,  $\text{Si}_4\text{Ph}_8\text{O}_2$ , cubes, prisms or needles from  $\text{Me}_2\text{CO}$ , m.  $245-6^\circ$  (rapid heating) or at  $190^\circ$  after cooling. This oxide is present in the most sol. fractions of the mono-oxide, but differs from this in that it does not give the rhomboidal oxide. The *rhomboidal oxide*,  $\text{Si}_4\text{Ph}_8\text{O}_2$ , isomeric with the second oxide described, is also found with the mono-oxide, from which it is readily sepd. by its slight soly. in  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_6$ . It seps. as rhomboids, fern-like masses or well defined pyramids, m.  $221-2^\circ$ . It has been obtained from both the satd. and the unsatd. hydrocarbon. The filtrate from the blue residue in the action of Na on  $\text{Ph}_2\text{SiCl}_2$  is evapd. to dryness, extd. with  $\text{Me}_2\text{CO}$ , leaving a colorless powder. The part freely sol. in cold  $\text{C}_6\text{H}_6$  is the *saturated silicohydrocarbon*,  $\text{Si}_4\text{Ph}_8$ , short, well defined rectangular prisms, does not m.  $400^\circ$ . Compared with the unsatd. hydrocarbon, it is very inert. It is completely decompd., however, by moist piperidine at  $90^\circ$ , giving diphenylsilicanediol, and tetraanhydrotetrakis(diphenylsilicanediol). The action of Br on a  $\text{CCl}_4$  soln. gives the rhomboidal oxide and condensation products of  $\text{Ph}_2\text{Si}(\text{OH})_2$ .  $\text{HNO}_3$  in boiling  $\text{AcOH}$  also gives the rhomboidal oxide. The diiodide,  $\text{Si}_4\text{Ph}_8\text{I}_2$ , treated with an excess of Na in boiling  $\text{C}_6\text{H}_6$ , gave about 60-70% unsatd. hydrocarbon. XXVI. Piperidine as an analytical reagent. *Ibid* 818-50.—The action of piperidine on Si compds. leads to the quant. evolution of H. This then furnishes a very convenient method of detg. the formulas of some of these complex compounds. A small quantity of the substance (0.1 g.) is placed in a test-tube together with a small tube containing piperidine (2-3 cc.) and the test-tube is connected to a long graduated tube partly immersed in a cylinder of water. When the air in the app. has acquired room temp. the piperidine is brought into contact with the Si compd. and the reaction is started by the application of heat. A brisk evolution of H sets in and after 1-50 min. is complete. A high degree of accuracy in measuring the vol. of H is unnecessary.

C. J. WEST

**Anilinolead compounds.** HJ. MANDAL. Univ. Upsala. *Ber.* 54B, 703-8(1921). — $\text{PbF}_2$  does not dissolve at all in  $\text{PhNH}_2$ ;  $\text{PbSO}_4$  and  $\text{Pb}_3(\text{PO}_4)_2$  enough to make it possible to detect Pb in the soln. with  $\text{H}_2\text{S}$ ;  $\text{Pb}(\text{NO}_3)_2$  dissolves somewhat more and on long standing the soln. deposits a small amt. of a white powder.  $\text{PbCl}_2$ ,  $\text{PbBr}_2$  and  $\text{PbI}_2$ , on the other hand, dissolve more easily and the following *addition products* cryst. from the solns. *Trianilinolead chloride*,  $\text{PbCl}_2 \cdot 3\text{PhNH}_2$ , from  $\text{PbCl}_2$  and  $\text{PhNH}_2$  warmed on the  $\text{H}_2\text{O}$  bath, filtered after about 1 hr., seeded (with crystals obtained by rubbing a few drops of the soln. on a watch glass and allowing to stand), filtered after 2 days and dried at  $15-6^\circ$ , best in the dark, felted needles,  $d_r$  1.98, decompd. into the components by  $\text{H}_2\text{O}$ , alc.,  $\text{Et}_2\text{O}$  or  $\text{CS}_2$ , loses  $\text{PhNH}_2$  at  $20-2^\circ$ , especially in the light (the loss is complete in 2 days); under  $\text{PhNH}_2$  it decomp.  $83-5^\circ$ . *Dianilinolead bromide*, prepd. like the chloride, felted needles,  $d_r$  2.47, slowly loses wt. at  $20-2^\circ$  for a few days when it becomes const., having changed into an egg-yellow compound  $3\text{PbBr}_2 \cdot 2\text{PhNH}_2$  which loses all its  $\text{PhNH}_2$  to alc. *Anilinolead iodide*, yellow needles,  $d_r$  3.50, slowly loses  $\text{PhNH}_2$  only at  $50^\circ$ , slowly with  $\text{H}_2\text{O}$ , quickly with alc. or  $\text{Et}_2\text{O}$ . A mixt. of  $\text{PbCl}_2$  and  $\text{PbBr}_2$  treated with  $\text{PhNH}_2$  on the  $\text{H}_2\text{O}$  bath gives the compound  $3\text{PbCl}_2 \cdot \text{PbBr}_2 \cdot 12\text{PhNH}_2$ , fine needles. In the same way is obtained the compound  $6\text{PbBr}_2 \cdot \text{PbI}_2 \cdot 14\text{PhNH}_2$ , fine needles, converted by alc. into the light yellow compound  $\text{PbI}_2 \cdot 6\text{PbBr}_2 \cdot 4\text{PhNH}_2$ . The compound  $3\text{PbBr}_2 \cdot \text{PbI}_2 \cdot 8\text{PhNH}_2$ , obtained at the b. p. of the  $\text{PhNH}_2$ , is converted by alc. into a yellow compound  $\text{PbI}_2 \cdot 3\text{PbBr}_2 \cdot 2\text{PhNH}_2$ .

CHAS. A. ROUILLER

**Cumulative effect of the chlorine atom and the methyl and sulfonyl chloride groups on substitution in the benzene nucleus.** I, II. WILLIAM DAVIES. Univ. Oxford.



*J. Chem. Soc.* 119, 853-75, 876-87(1921).—D. has undertaken the study of the nitration of certain  $\text{MeClC}_6\text{H}_4\text{SO}_3\text{Cl}$ . The *p*-directing influence of the Cl atom is about 3 times as great as the combined *o*- and *m*-directing influences of the Me and  $\text{SO}_3\text{Cl}$  groups. resp. In predicting the position chiefly taken up by the new 4th substituent it is necessary to bear in mind the relative directing power of the 2 positive substituents. Even the difference in power of these 2 groups may be great enough to overwhelm the effect of the 3rd negative group. This does not apply to the particular case of substitution with Cl. 1,2,4- $\text{MeClC}_6\text{H}_4\text{SO}_3\text{Cl}$  (A) (German pat. 145908; Wynne and Bruce, *J. Chem. Soc.* 73, 764) was prepd. by melting 311 g. *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{Cl}$  with 6 g.  $\text{SbCl}_3$  and introducing Cl till the gain in wt. was 57 g. Extd. with  $\text{H}_2\text{O}$ , then  $\text{C}_6\text{H}_6$ , 276 g. were obtained, m.  $38-8^\circ$ . 100 g. A were gradually added to a cold mixt. of 50 cc.  $\text{HNO}_3$  (d. 1.5) and 125 cc.  $\text{H}_2\text{SO}_4$  and stirred for 2 hrs., the temp. being kept at  $20-30^\circ$ . The isomerides were sepd. by crystg. from light petroleum (b.  $60-80^\circ$ ). The less sol. part is 2-chloro-5-nitro-*p*-toluenesulfonyl chloride,  $\text{C}_7\text{H}_5\text{O}_4\text{NClS}$  (B), large prisms, m.  $99.2^\circ$ . The more sol. portion is 2-chloro-6-nitro-*p*-toluenesulfonyl chloride (C), long needles, m.  $70^\circ$ . The eutectic mixt. of B and C m.  $50.9^\circ$  and contains 63.3% C. A table is given showing the 1st and 2nd solidification points of a number of mixts., from which a m. p. curve was constructed. From this it was detd. that the nitration mixt. contains 25.5% C. When the nitration was carried out at  $65-70^\circ$ , the % of C was about 35. Amide of B, small needles, m.  $181^\circ$ . 2-Chloro-5-nitro-*p*-toluenesulfonic acid, by hydrolyzing B with concd.  $\text{HCl}$  in a sealed tube, thick clusters of small non-deliquescent needles, m.  $123-8^\circ$ . Sodium salt,  $\text{C}_7\text{H}_4\text{O}_4\text{NClSNa} \cdot 2\text{H}_2\text{O}$  (D), by boiling B with a slight excess of  $\text{NaOH}$ , pale yellow needles. Barium salt, scales with 2  $\text{H}_2\text{O}$ . 5 g. B in a mixt. of 50 cc. hot  $\text{H}_2\text{O}$  and 25 cc. glacial  $\text{AcOH}$ , treated gradually with 7 g. Fe filings and heated for 1 hr., gave 6-chloro-*m*-toluidine-4-sulfonic acid, thin, small plates, which turn red on exposure to light and air.  $\text{Br} \cdot \text{H}_2\text{O}$  gives 6-chloro-2,4-dibromo-*m*-toluidine, long needles from alc., m.  $99.5^\circ$ . 2-Chloro-5-nitro-*p*-cresol (E), by hydrolysis of B with 6 mols. *N*  $\text{NaOH}$ , in 22% yield, sublimes in long, thin, lemon-colored needles, m.  $71^\circ$ . It is very volatile with steam and has a faint odor of *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$ . A colorless aq. soln. of the cresol (1 : 100,000) becomes yellow on the addition of  $\text{NaOH}$  and colorless on acidification. Benzoate, needles, m.  $129^\circ$ . Sodium salt, amorphous red powder, slightly sol. in boiling  $\text{H}_2\text{O}$ , by which it is slowly hydrolyzed. Lithium salt, orange-red amorphous powder, slightly sol. in  $\text{H}_2\text{O}$ . Potassium salt, long, anhydrous crimson needles, very sol. in boiling  $\text{H}_2\text{O}$ . Ammonium salt, long, orange-red needles, very sol. in hot dil.  $\text{NH}_4\text{OH}$ . The Rb and Cs salts are not pptd. by double decompn. of the K salt. E was synthesized as follows:  $p\text{-O}_2\text{NC}_6\text{H}_4\text{Me} \rightarrow 1,2,4\text{-MeClC}_6\text{H}_4\text{NO}_2 \rightarrow 1,2,4\text{-MeClC}_6\text{H}_4\text{NH}_2 \rightarrow 1,2,4\text{-MeClC}_6\text{H}_4\text{NHAc}$ , which, when 10 g. are gradually added to 40 cc.  $\text{HNO}_3$  (d. 1.5), gave 2-chloro-3,5-dinitroaceto-*p*-toluidide, leaflets, m.  $238^\circ$ . Hydrolysis with cold  $\text{H}_2\text{SO}_4$  gave 2-chloro-3,5-dinitro-*p*-toluidine, thin, golden yellow needles, m.  $137^\circ$ . When the nitration was carried out at  $15^\circ$  with a small excess of  $\text{HNO}_3$ , 1,2,4,5- $\text{C}_6\text{H}_2\text{MeCl}(\text{NH}_2)_2\text{NO}_2$  was obtained in good yield, which, when diazotized and slowly added to a boiling soln. of 20 g.  $\text{CuSO}_4$ , 45 g.  $\text{Na}_2\text{SO}_4$ , 30 cc. concd.  $\text{H}_2\text{SO}_4$  and 100 cc.  $\text{H}_2\text{O}$ , gave E. A small amt. of E is formed when D is heated with 10% aq.  $\text{NH}_3$  for 36 hrs. at  $135-145^\circ$  (sealed tube). Amide of C, shining scales from  $\text{H}_2\text{O}$  or needles from alc., m.  $182^\circ$ . 2-Chloro-6-nitro-*p*-toluenesulfonic acid, deliquescent plates, very sol. in  $\text{H}_2\text{O}$ . Sodium salt, anhydrous microplates, almost insol. in boiling 99% alc.; potassium salt, colorless laminas; barium salt, leaflets from  $\text{H}_2\text{O}$  with 3  $\text{H}_2\text{O}$  of crystn., glistening laminas from alc. The constitution was detd. by the action of  $\text{NaOH}$  on the Na salt. 2,6-Dichloro-*p*-toluenesulfonyl chloride, by passing Cl into a fused mixt. of 125 g. 1,2,4- $\text{MeClC}_6\text{H}_4\text{SO}_3\text{Cl}$  and 5 g.  $\text{SbCl}_3$  at  $60-70^\circ$  for 2 hrs. (gain in wt., 19.2 g.), plates from light petroleum, m.  $69^\circ$ ; yield, 66%. The acid crystals



in deliquescent plates, very sol. in  $H_2O$ . *Amide*, shining scales, m.  $191^\circ$ . *Sodium salt*,  $C_7H_5O_2Cl_2SNa \cdot H_2O$ , clusters of fan-like, divergent needles, readily sol. in hot  $H_2O$ . *Barium salt*, thin, minute, silky needles with 3  $H_2O$ . Hydrolysis of the Na salt gave 2,6- $Cl_2C_6H_3Me$ . 2,5-Dichloro-*p*-toluenesulfonyl chloride is also formed in the above chlorination. A further study has been made to det. whether the combined *p*- and *m*-directing influences of the Me and  $SO_2Cl$  groups would be overpowered by the Cl. In 1,2,6- $C_6H_3Me(SO_2Cl)Cl$ , the Cl atom has a slightly smaller orientating effect than the other 2 groups acting together, so far as substitution by the  $NO_2$  group is concerned. Since in 1,2,6- $C_6H_3MeClNO_2$  the Cl has an almost overwhelming directive influence, it follows that the  $SO_2Cl$  group has a more powerful orientating effect than the  $NO_2$  group. 6-Chloro-*o*-toluenesulfonyl chloride (F),  $C_7H_4O_2Cl_2S$ , by the chlorination of *o*- $MeC_6H_4SO_2Cl$  in the presence of 1%  $SbCl_5$ , large, thick prisms or plates, m.  $72^\circ$ . The constitution was established by converting it into *o*- $ClC_6H_4CO_2H$ . The free acid forms thin lustrous non-deliquescent laminas, m.  $60-70^\circ$ . *Amide*, glistening scales, m.  $180^\circ$ . *Sodium salt*, large glistening laminas with 1  $H_2O$ . *Barium salt*, small lustrous flakes, with 1  $H_2O$ . When 10.2 g. of the amide and 4 g.  $NaOH$  in 1000 cc. boiling  $H_2O$  (through which  $CO_2$  was slowly passed) were treated with 17.4 g.  $KMnO_4$  in 250 cc.  $H_2O$  the  $KMnO_4$  was decolorized after 7 hrs. and 62% of "chlorosaccharin" (6-chloro-*o*-benzoic sulfonide) were obtained, small shining plates, m.  $210-2^\circ$ . It is about half as sweet as saccharin but has an astringent taste, except in very great diln. Nitration of F (50 g. F, 150 cc.  $H_2SO_4$ , 45 cc.  $HNO_3$ ) gave a mixt. of 3- and 4- $NO_2$  derivs. sepd. by transforming to the Ba salt and extg. with 99% alc., which removes the 3- $NO_2$  deriv. 6-Chloro-3-nitro-*o*-toluenesulfonyl chloride,  $C_7H_3O_2NCl_2S$ , long needles, m.  $80^\circ$ , is obtained in 40% yield. Acid, very deliquescent micropisms, easily sol. in  $H_2O$ . Sulfonamide, minute needles, m.  $181^\circ$ . *Sodium salt*, needles, with 4  $H_2O$ , very sol. in  $H_2O$  or hot and cold alc., decomp.  $140-50^\circ$ . *Barium salt*, compact clusters of microneedles from alc., very sol. in hot or cold  $H_2O$  and alc., contains 7  $H_2O$  from  $H_2O$ , decomp.  $140^\circ$ . The constitution of the chloride was detd. by conversion into 1,2,3,6- $C_6H_2Me(OH)(NO_2)Cl$  (Ber. 37, 1013). 6-Chloro-4-nitro-*o*-toluenesulfonyl chloride, large thick prisms or thin laminas, m.  $63-4^\circ$ . Acid, flattened needles. *Amide*,  $C_7H_3O_2N_2ClS$ , minute needles, m.  $161^\circ$ . *Sodium salt*, plates or needles with 1  $H_2O$ . *Barium salt*, needles with 1  $H_2O$ . C. J. WEST

**Problem of the valence of sulfur.** IV. Arylsulfur thiocyanates. HANS LECHER AND KURT SIMON. Akad. Wiss. München. Ber. 54B, 632-8 (1921); cf. C. A. 14, 3079; Söderbäck, C. A. 14, 1808.—In S's "compound halogen," thiocyanogen, the halogen-like valence doubtless proceeds from the S; in all halogen-like reactions of free thiocyanogen are formed derivs. with the grouping  $-SC:N$ . L. and S. therefore believe that in  $S_2(CN)_2$ , the S atoms of the two SCN complexes are homopolarically united by the same arrangement of electrons as the 2 atoms in the  $Cl_2$  mol. The present investigation deals with the question whether compds. of the type  $ArSSCN$  are "arylsulfur disulfides" with homopolaric union or "arylsulfur thiocyanates" with a heteropolaric union between the S atoms. In the first case such compds. might possibly show the halogen-like reactions of free thiocyanogen; in the second they ought to bear a close analogy to Zincke's arylsulfur chlorides. The latter proved to be the case. From 3.8 g. *o*- $O_2NC_6H_4SCl$  in 40 cc.  $C_6H_6$  shaken 40 hrs. with the calcd. amt. of  $KSCN$ , filtered from the KCl and concd. is quant. obtained *o*-nitrophenylsulfur thiocyanate (A), yellow crystals from  $CCl_4$ , m.  $93-4^\circ$ , easily sol. in liquid  $SO_2$ , the satd. soln. giving with anhydrous  $FeCl_3$  a distinct red color. A gives no  $Ag_2S$  with boiling alc.  $NH_3$ ,  $AgNO_3$  or  $PbS$  with boiling alk. Pb soln.; on heating it evolves the same characteristic odor as the chloride and on Pt foil it melts and then deflagrates harmlessly; heated 3 hrs. in  $C_6H_6$  at  $200^\circ$  it undergoes deep-seated decompn. It is also obtained in 2.6



g. yield from 1 cc. Br in 40 cc. cold Et<sub>2</sub>O quickly treated with 7.5 g. white Pb(SCN)<sub>2</sub>, immediately shaken to disappearance of the Br color (about 0.5 hr.), filtered from the Pb salts (which are washed with 60 cc. Et<sub>2</sub>O), slowly treated in the cold with 3.1 g. *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SH in Et<sub>2</sub>O and cooled to -18°; the mother liquors yield another 0.5 g. When a vigorous stream of dry NH<sub>3</sub> was passed through 50 cc. cold C<sub>6</sub>H<sub>6</sub> and at the same time 4.2 g. A in 50 cc. C<sub>6</sub>H<sub>6</sub> was dropped in, a liquid mixt. of NH<sub>4</sub>SCN and NH<sub>3</sub> sepd. under the C<sub>6</sub>H<sub>6</sub>; ice H<sub>2</sub>O removed 1.4 g. NH<sub>4</sub>SCN, and the dried C<sub>6</sub>H<sub>6</sub> layer on evapn. yielded 3.25 g. *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SNH<sub>2</sub>, m. 124-5°. From 2.1 g. A in 30 cc. C<sub>6</sub>H<sub>6</sub> allowed to stand 45 min. with 3 g. PhNMe<sub>2</sub>, then boiled 15 min. under a reflux, cooled, shaken with soda and freed from C<sub>6</sub>H<sub>6</sub> and PhNMe<sub>2</sub> with steam is obtained 2.3 g. *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, m. 188°. PhSH (2.2 g.) in 10 cc. C<sub>6</sub>H<sub>6</sub> slowly treated with 4.2 g. A in 40 cc. C<sub>6</sub>H<sub>6</sub>, freed from HSCN by washing with H<sub>2</sub>O, soda and H<sub>2</sub>O, dried, evapd. and extd. with Et<sub>2</sub>O left undissolved 0.4 g. (*o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub> while the Et<sub>2</sub>O ext. yielded a mixt. of Ph<sub>2</sub>S<sub>2</sub> and 1.2 g. *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SPh. Although *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCl is completely hydrolyzed when shaken 4-5 hrs. with 20 parts H<sub>2</sub>O and glass beads A is practically unchanged under the same conditions. As Ph<sub>3</sub>CSCN (Elbs, *Ber.* 17, 700(1884)) shows a similar stability towards H<sub>2</sub>O, it was prepd. by shaking 9.3 g. Ph<sub>3</sub>CCl in 100 cc. C<sub>6</sub>H<sub>6</sub> 2 days with the equiv. amt. of powdered KSCN; it seps. from ligroin in crystals, m. 137°, b. 203°, sublimes markedly *in vacuo* at a high temp., dissolves in concd. H<sub>2</sub>SO<sub>4</sub> with the same halochromism as the chloride, is unchanged by shaking 24 hrs. with 50 parts H<sub>2</sub>O or by treating 1 hr. in boiling C<sub>6</sub>H<sub>6</sub> with NH<sub>3</sub>, forms no PbS nor Ag<sub>2</sub>S with boiling alk. Pb soln. or NH<sub>3</sub>-AgNO<sub>3</sub>; contrary to E.'s statement, it cannot be distd. without decompn. under atm. pressure and it partially decompn. in C<sub>6</sub>H<sub>6</sub> at 200°.

CHAS. A. ROUVIER

**Artificial and natural humic acids.** WILHELM ELLER. *Jena. Brennstoff Chem.* 2, 129-33(1921); cf. C. A. 15, 83(1921). The humic-like substance prepd. by E. by the action of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and KOH on pyrocatechol, quinone or quino, corresponds well with the empirical formula C<sub>12</sub>H<sub>6</sub>O<sub>5</sub>, and the author regards it as a binol.

polymerization product of hydroxyquinone,  $\text{O} \begin{array}{c} \text{C}_6\text{H}_4\text{OH} \\ \text{O} \end{array} \text{O} \begin{array}{c} \text{C}_6\text{H}_4\text{OH} \\ \text{O} \end{array} \text{O}$ . On chlorination a small quantity of chloranil is always formed, and the nitration product is not decompd. by boiling with KOH. The humic acid may easily be methylated, acetylated or benzoylated, indicating the presence of phenolic OH, and the fact that with Br and KOH, CHBr<sub>3</sub> and CBr<sub>4</sub> are formed is further evidence. The evidence for the binol. structure is not so convincing; Stoltzenberg found that when benzoquinone was boiled for a long time in water, dark brown amorphous masses of (C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub> were formed, and that this passed easily into the humic acid C<sub>12</sub>H<sub>6</sub>O<sub>5</sub>. The presence of a furan grouping is thought to be improbable. The present product cannot be compared with the natural humic acids by means of mol. wt. or m. p.; the C content corresponds well, but the H content of the natural acids is usually reported higher, owing, in E.'s opinion, to the difficulty of drying them thoroughly without decompn. The phys. and chem. properties correspond well. The high absorption capacity for NH<sub>3</sub> is noted, with the opinion that it accounts for earlier statements that humic acid contains N. E. does not exclude the possibility that the natural humic acids may be mixts. containing analogous compds. of higher mol. wt.

W. B. V.

**Oxidation of aromatic hydrocarbons under pressure.** HANS SCHRADER. *Ger. Abhand. Kenntn. Kohle* 4, 210-11(1920). The autoxidation of aromatic hydrocarbons by air under increased pressure and in the presence of an alk. soln. takes place so readily at a comparatively low temp. (about 200°) that it is possible to obtain oxidation products in considerable quantity in the course of a few hrs. In the series, benzene, naphthalene, anthracene, the autoxidizability increases with increasing number of nuclei; with the



homologs of benzene, it increases with the number of aliphatic groups.  $C_6H_6$  and  $PhCl$  are not noticeably affected at  $210^\circ$ , but action begins to be obvious at  $260^\circ$ .  $C_{10}H_8$  is scarcely changed at  $210^\circ$ , but is markedly oxidized, mainly to phthalic acid, at  $260^\circ$ ; anthracene is distinctly attacked at  $210^\circ$ , and completely changed at  $260^\circ$ , being transformed mainly into anthraquinone and smaller amts. of naphthalene-2, 3-dicarboxylic and phthalic acids. With the homologs of benzene, the chief reaction consists in the complete or partial conversion of the aliphatic residues into  $CO_2H$  groups. Small amts. of  $BzOH$  are produced from  $PhMe$  or  $PhEt$  at  $210^\circ$ . The xylenes are more readily changed and pass into the corresponding toluic and phthalic acids. *p*-Cymene is still more readily oxidized, yielding, among other products, cumic, toluic, and terephthalic acids. The three chlorotoluenes are noticeably more stable than the parent substance, but, at  $260^\circ$ , are converted into the corresponding chlorobenzoic acids. Under the exptl. conditions, all the aromatic hydrocarbons are oxidized to oxalic, acetic, formic, and carbonic acids to a greater or less extent. The intermediate formation of aldehydes is established. The mechanism of the oxidative process is discussed and a review is given of the literature on the oxidation of aromatic hydrocarbons by air or gaseous  $O$ . The phenomena of autoxidation are of considerable importance in connection with the use of aromatic hydrocarbons in internal-combustion engines. The temp. of ignition, autoxidizability and stability of a compd. are closely related to one another.

J. C. S.

**Siam benzoin.** II. *Siaresinolic acid*. F. REINITZER. *Arch. Pharm.* **259**, 1-6(1921); cf. *C. A.* **9**, 121.—Examin. of the crystals isolated in various ways both from the tear crusts and the tears themselves showed the substance to be a *d*-siaresinolic acid, m.  $260^\circ$  ( $260-70^\circ$  according to Zinke and Lieb, *C. A.* **13**, 79),  $[\alpha]_D^{25.6}$   $37.793^\circ$  in  $EtOH$ . The acid has the compn.  $C_{17}H_{16}O_8$ , yielding with  $AcOH$  the compd.  $C_{18}H_{16}O_4 \cdot C_2H_4O_2$ . Na and K salts were prepd. which with other derivs. are more minutely described by Zinke and Lieb. III. **Properties and constitution of lubanol benzoate.** *Ibid.* 60-9.—Lubanol benzoate (cf. *C. A.* **9**, 121) crystals in plates m.  $72.8^\circ$ , and contains 1 MeO group. When exposed to warm air it readily suffers oxidation, thereby passing through color changes very like those yielded by the crude resin. On heating to  $120-40^\circ$  it loses  $BzOH$ , while at higher temps. it evolves the odor of carnations followed by that of guaiacol. A comprehensive series of color changes is given. The optically inactive benzoate suffers hydrolysis in both acid and alk. soln. Isolation of the pure lubanol was found impossible thus far on account of its marked susceptibility to change, especially in alk. soln. The prepn. of a dibenzoate and a dibromobenzoate leads to the conclusion that lubanol is identical with or closely related to coniferyl alc. However, until a cryst. specimen of lubanol is obtained, no definite decision can be reached on this question, although the color reactions of the benzoate harmonize with this view.

W. O. E.

**Derivatives of anesthesin (ethyl *p*-aminobenzoate).** H. THOMS AND K. RITSERT. *Ber. pharm. Ges.* **31**, 65-75(1921); *J. Chem. Soc.* **120**, I, 343-4.—The undermentioned derivs. of  $p\text{-H}_2N\text{C}_6\text{H}_4\text{CO}_2\text{Et}$ , in which the H atom of the  $NH_2$  group is replaced by various + and - groups, were prepd. with the object of detg. the effect of such substitution on the anesthetic properties of the ester. In general, the physiol. action was much reduced by the substitution of amino H atoms, and entirely disappeared with the introduction of negative groups. Only in the case of *p*-hydrazinobenzoic acid, where a 2nd  $NH_2$  group is substituted for a H atom, was the anesthetic action at all comparable to that of anesthesin itself. The following derivs. are described: ethyl *p*-*N*-allylthiocarbamidobenzoate, prepd. by the action of allylthiocarbamide on anesthesin, forms colorless needles, m.  $92^\circ$ , and is but feebly anesthetic. Ethyl *p*-*N*-allylcarbamidobenzoate (from the preceding compd. by treatment with  $HgO$ ), forms



leaflets, m. 120°, feebly anesthetic. *Ethyl p-β,γ-dibromopropylthiocarbamidobenzoate*,  $\text{EtCO}_2\text{C}_6\text{H}_4\text{NHC(S)NHCH}_2\text{CHBrCH}_2\text{Br}$  (by the action of Br on the allyl deriv.), needles, m. 146.5°, non-anesthetic. *Ethyl p-β,γ-dibromopropylcarbamidobenzoate*, similarly prepd. from the allyl deriv., needles, m. 146°, non-anesthetic. *Ethyl p-hydrazinobenzoate*,  $\text{EtCO}_2\text{C}_6\text{H}_4\text{NHNH}_2$ , prepd. by reducing diazotized anesthesin, leaflets m. 114°, slightly sol. in warm  $\text{H}_2\text{O}$ , gives a sol. *hydrochloride*, m. 214° (decompn.), both good anesthetics. The hydrazine readily condenses with aldehydes, ketones, etc., and the following derivs. are described: *Ethyl p-isopropylidenhydrazinobenzoate*,  $\text{EtCO}_2\text{C}_6\text{H}_4\text{NHN:CMe}_2$ , m. 112°, *ethyl p-benzylidenhydrazinobenzoate*,  $\text{EtCO}_2\text{C}_6\text{H}_4\text{NHN:CHPh}$ , m. 160°. *Ethyl p-cinnamylidenhydrazinobenzoate*, m. 156.5°. *Ethyl glucosazone-p,p-dibenzoate*, m. 198°, *ethyl acetoacetate p-carbethoxyphenylhydrazone*, yellow needles, m. 107°, on heating at 130–40° is converted into *ethyl 4-methylpyrazolone-1-benzoate*, needles, m. 145°. None of the above hydrazine derivs. is anesthetic. *Ethyl p-urelhanobenzoate*,  $\text{EtCO}_2\text{C}_6\text{H}_4\text{HNCO}_2\text{Et}$ , by the action of  $\text{ClCO}_2\text{Et}$ , needles, m. 130.5°, feebly anesthetic. *p-Carbethoxyphenylaminoacetic acid*, glistening leaflets, m. 163°, and *ethyl p-nitrobenzoyl-p-aminobenzoate*, yellowish rhombs, m. 211°, neither of which is anesthetic. W. O. E.

**Influencing the effectiveness of catalyzers.** KARL W. ROSENMUND AND F. ZETZSCHE. II. The reduction of acid chlorides to alcohol and ester. KARL W. ROSENMUND AND F. HEISE. Univ. Berlin. *Ber.* 54B, 638–47(1921); cf. *C. A.* 15, 2435.—In the first paper was described a method which seemed to make it possible to influence catalyzers in general, both as to their degree of activity and as to their way of acting, but the exptl. material was too meager to allow of judging as to the significance of the general principle involved in the method. In the first place it might be objected that, as the result of the very great reactivity of the Cl in acid chlorides, its replacement takes place with such ease that the repression of further reactions may be ascribed chiefly to this reactivity and that under less favorable conditions it would not be possible to influence the catalyzer. A good test of this is furnished by a further study of the acid chloride reduction, which, when the catalyst is not influenced, leads through the aldehyde and the alc. to the hydrocarbon, whereas it has been found that the catalyst can be so influenced that chiefly the product of the second stage, the alc., is formed. In order to do this, the catalyzer must be put into a condition where it can bring about 2 different reactions, viz., (1) a substitution reaction consisting in the exchange of the halogen for H, and (2) an addition reaction, whereby the aldehyde is converted into the alc., and at the same time hinder (3) the reduction of the alc. to the hydrocarbon. As the ease with which (2) and (3) are brought about does not differ greatly, this involves a rather fine gradation of the catalytic activity. The alc. formed as the result of (2) reacts with the unchanged chloride, so that the ester might be expected as the end product of the desired reaction. In the course of the investigation, however, it was found that the ester is also changed by the catalyzer, so a special study had to be made to eliminate this reaction. Starting with the reduction of  $\text{BzCl}$  in xylene with H and Pd, which gave about 45% high boiling hydrocarbons (chiefly  $(\text{PhCH}_2)_2$ ), 16%  $\text{BzOH}$ , 15%  $\text{PhCH}_2\text{OBz}$  and the remainder  $\text{PhMe}$ , it was first attempted so to influence the catalyzer as to increase the yield of ester. Diminution of the pressure, a purely physical measure, increased the ester output to 22–37% and diminished that of high boiling hydrocarbons to 22–3%. Attention was then turned to the addition of foreign substances, especially N and O compds. in which, owing to the possibility of a change of valence (from 3 to 5 in the case of N, from 2 to 4 in that of O), the development of secondary valences and the formation of the "complexes" required by the new theory might be looked for. Of 2 such substances tried, quinoline (A) and xanthone (B), each worked differently. Minimal amts. of A produce the disappearance of the nor-



mal products, hydrocarbon, acid and ester, and the formation chiefly of alc., then of aldehyde and of the ether, while B acts as hoped for, changing the course of the reaction quant., not qual. The fact that considerable amts. of acid always accompanied the ester led to the belief that there might be a connection between the two and it was found that, as a matter of fact, when pure  $\text{PhCH}_2\text{OBz}$  is hydrogenated in xylene, it decomps. into  $\text{BzOH}$  and  $\text{PhMe}$ . This observation makes it possible to explain the formation of the by-products (a cryst. substance m.  $106-7^\circ$ ,  $3,4,5\text{-(MeO)}_3\text{C}_6\text{H}_2\text{CO}_2\text{H}$  and  $1,2,3\text{-C}_6\text{H}_3(\text{OMe})_3$ ) obtained by Spith (C. A. 14, 1114) in the prepn. of  $(\text{MeO})_3\text{-C}_6\text{H}_2\text{CHO}$ ; his cryst. substance is *trimethylgallyl trimethylgallate* and decomps. into  $(\text{MeO})_3\text{C}_6\text{H}_2\text{CO}_2\text{H}$ ,  $\text{C}_6\text{H}_3(\text{OMe})_3$  and  $\text{CH}_4$ . R. and H. in the hydrogenation of  $\text{MeOC}_6\text{H}_4\text{COCl}$  obtained  $\text{PhOMe}$  besides  $p\text{-MeOC}_6\text{H}_4\text{Me}$ . Having discovered this reduction cleavage, means of eliminating it were investigated and it was found that it could be almost completely repressed by the use of  $\text{PhMe}$ . The results obtained in the hydrogenation of  $\text{BzCl}$  are summarized in the following table.

Pressure, additions, etc.	Amt. used g		Catalyzr.	Time, Hrs	BzOH.	BzH.	Yield. %.			
	BzCl.	Solvent					PhCH <sub>2</sub> OH.	PhCH <sub>2</sub> OBz.	Hydrocarb.	(PhCH <sub>2</sub> ) <sub>2</sub> O.
Solvent — xylene.										
—	10	40	3	7	16	—	—	15	45	—
560 mm.	10	40	3	7.5	14	10	—	19	40	—
460 "	10	40	3	7.5	15	11	—	25	31	—
360 "	10	40	3	7.5	7	9	—	37	22	—
1 mg. quinoline	5	20	1.5	5	—	12	40	—	—	12
2 "	5	20	1.5	5	—	30	24	—	—	12
5 "	5	20	1.5	5.5	—	42	8	—	—	20
10 "	5	20	1.5	6.5	—	42	16	—	—	10
2 "	5	20	1.5	6.5	—	55	7	—	—	6
20 mg. xanthone	5	20	1.5	5	20	—	—	24	30	—
60 "	5	20	1.5	7	25	—	—	13	30	—
Solvent — toluene.										
—	5	20	1.5	5	6	—	—	45	18	—
660 mm.	5	20	1.5	7	11	—	—	51	10	—
20 mg. xanthone	5	20	1.5	5.5	6	—	—	53	14	—
50 "	5	20	1.5	6.5	5	4	—	60	10	—
100 "	5	20	1.5	6.5	5	8	—	53	10	—
1 mg. quinoline	5	20	1.5	5	—	60	11	—	—	10
0.5 mg. "	5	20	1.5	7	—	20	12	35	7	—
0.4 "	5	20	1.5	6.5	—	27	—	40	—	10
0.3 "	5	20	1.5	8	3	3	20	35	—	5
0.2 "	5	20	1.5	6.5	3	4	5	43	—	10

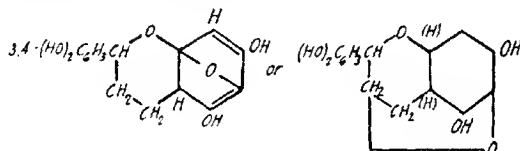
CHAS. A. ROUILLER

Action of phosphoric oxide on salicylic acid. A. LANGER. *Apoth. Ztg.* 36, 42 (1921); *J. Chem. Soc.* 120, 1, 345.—When salicylmetaphosphoric acid is heated with  $\text{PhOH}$  at  $150^\circ$ , salol red, described by Zimmermann (*Apoth. Ztg.* 36, 17) as well as the similar hydroxyphenylhydroxydiphenylcarbinols, occur in greater amts. than salol, which can be obtained pure by repeated treatment with hot  $\text{NaOH}$  soln. The



dyes thus obtained dye wool directly. *Salol red*,  $C_{15}H_{10}O_4$ , is a reddish brown powder, m.  $116-9^\circ$ , sol. like phenolphthalein in alkalis. The compound,  $C_{15}H_{10}O_4$ , obtained with resorcinol is a metallic looking powder, but crystals in reddish yellow spikelets from alc. and m.  $209^\circ$ . The compound,  $C_{23}H_{12}O_{16} \cdot 3H_2O$ , from pyrogallol forms reddish violet plates, m.  $145^\circ$ . The deriv. prepd. with  $PhNH_2$  (2 mols.) gives in glacial AcOH with  $K_2Cr_2O_7$  an acid-stable blue dye insol. in  $H_2O$  and alkalis. The Na salt of the sulfonic acid is sol. in  $H_2O$  and dil. alc. W. O. E.

**Catechol.** ASTRID CLEVE v. EULER. *Svensk. Kem. Tid.* 33, 88-98(1921).—The history of catechol is briefly reviewed up to the contribution of Kostanecki in 1906 (*C. A.* 1, 560), which is considered in more detail than the foregoing. K. proposed a constitutional formula for catechol which replaced the one given by Perkin (1902) and was accepted by P. himself. v. E. does not consider the K. formula tenable. It does not satisfy all of the 13 established facts pertaining to this compd. P.'s formula, on the other hand, will do so if an O bridge is introduced in its phloroglucinol group, and the following are therefore proposed by v. E.:



The validity of the K. formula has recently been challenged by Freudenberg (*C. A.* 15, 78), who attacked it from the biological angle. His modification of the formula to conform with analogous series in plants (e. g., flavonins) is not considered fortunate in that it fails in the following particulars. It allows the sepn. of OH as  $H_2O$  and it permits di-Br and penta-Me derivatives. The new formula makes possible a simple change from phloroglucinol to hydroxyphloroglucinol—the hydroxypyrogallol group—and thereby explains the transformation of catechol to the amorphous tannin substance. v. E. holds that strictly speaking there are no phloroglucinol tannins. The substances are formed by a rearrangement of three phenyloxy groups as, e. g., in gallic acid. Such rearrangement is as tenable for catechol as for the closely related cyanomacrlurin.

A. R. ROSE

**Resolution of racemic acids by optically active alcohols. II. The resolution of atrolactic and  $\alpha$ -hydroxy- $\beta$ -phenylpropionic acids by *l*-menthol.** HENRY WREN AND EDWARD WRIGHT. Municipal Tech. Inst., Belfast. *J. Chem. Soc.* 119, 798-803 (1921); cf. *C. A.* 14, 3220. *l*-Menthyl *dl*-atrolactate, b<sub>76</sub>  $190^\circ$ ,  $[\alpha]_D^{20}$  in  $CHCl_3$  -67.5°, seeded with the *l*-isomer, was cooled for several days and the pasty mass spread on porous earthenware and then on filter paper; the *d*-isomer was mainly adsorbed, giving a product m.  $53.5-4.5^\circ$  (pure *l*-isomer m.  $55.5-6^\circ$ ) and  $[\alpha]_D^{20}$  -97.5° (pure, -1027°). Hydrolysis and crystn. from  $C_6H_6$  gave pure *l*-atrolactic acid. The resolution is more readily effected by crystn. from light petroleum at  $-18^\circ$  (43 g. *dl*-ester gave 1.7 g. pure *l*-ester). *l*-Menthyl *d*-atrolactate,  $C_{10}H_{12}O_4$ , by heating the acid and alc. for 20 hrs. at  $100^\circ$  with a little concd.  $H_2SO_4$ , viscous liquid, b<sub>60</sub>  $154-5^\circ$ ,  $[\alpha]_D^{20}$  -41.3° in  $CHCl_3$ ,  $[\alpha]_D^{25}$  -58.8° in EtOH. *d*-PhCH<sub>2</sub>CH(OH)CO<sub>2</sub>H was also resolved by cryst. the esters from light petroleum or from 96% EtOH, the *d*-ester crystalg. out. The mother liquor, on hydrolysis, gave the *l*-acid. *l*-Menthyl *l*- $\alpha$ -hydroxy- $\beta$ -phenylpropionate,  $C_{15}H_{18}O_4$ , b<sub>12</sub>  $212-4^\circ$ ,  $[\alpha]_D^{20}$  in  $CHCl_3$  -80.5°, in EtOH -47.4°. *l*-Bornyl *d*- $\alpha$ -hydroxy- $\beta$ -phenylpropionate,  $C_{17}H_{22}O_4$ , b<sub>11</sub>  $209^\circ$ ,  $[\alpha]_D^{20}$  in EtOH -36.7°,  $[\alpha]_D^{25}$  in  $CHCl_3$  -4.8°. *l*-Bornyl *l*- $\alpha$ -hydroxy- $\beta$ -phenylpropionate, pale yellow, viscous oil,



b, 203.5°,  $[\alpha]_D^{17}$  in EtOH  $-16.5^\circ$ , in  $\text{CHCl}_3$   $-49.9^\circ$ . *l*-Bornyl *dl*- $\alpha$ -hydroxy- $\beta$ -phenylpropionic acid, viscous liquid,  $b_D$  213–4°,  $[\alpha]_D^{12}$   $-26.1^\circ$  in EtOH. Attempts to resolve *d*-PhCH(OH)CH<sub>2</sub>CO<sub>2</sub>H by means of *l*-menthol showed that the acid was readily changed in the presence of mineral acid and the esters invariably contained *l*-menthyl cinnamate.

C. J. WEST

**Styrene from ethylbenzene.** JULIUS V. BRAUN AND KARL MÖLDÄNKE. Landw. Hochschule Berlin. *Ber.* 54B, 618–9(1921); cf. *C. A.* 15, 2866.—When PhEt at 145–55° is treated with 2 mols. Br (for 50 g. PhEt and 140 g. Br 1.5 hrs. are required) and is immediately distd. it gives 110 g. of PhCHBrCH<sub>2</sub>Br,  $b_D$  133°,  $m$ . 72°; when this is treated in Et<sub>2</sub>O with 1 atom Mg in small portions, heated a short time on the H<sub>2</sub>O bath and worked up in the usual way it gives 70% PhCH:CH<sub>2</sub>,  $b$ . 146°, and a small residue containing a little Br and partly solidifying on cooling; it apparently contains the so-called "liquid distyrene." Towards Zn, PhCHBrCH<sub>2</sub>Br behaves just like dibromotetralin; in Et<sub>2</sub>O or Me<sub>2</sub>CO the reaction is very vigorous, the soln. becomes yellow to brown and the products are almost free from Br but on distn. yield only minimal amts. of PhCH:CH<sub>2</sub> below 200°; the rest consists of high boiling polymers of PhCH:CH<sub>2</sub>, probably mixts. of di- and metastyrene.

CHAS. A. ROULLER

**Determination of the composition of mixtures of eugenyl and isoeugenyl benzoates by means of melting points.** PHYLLIS VIOLET McKIE. Univ. College North Wales. *J. Chem. Soc.* 119, 777–9(1921).—The compn. of the mixt. of eugenol and isoeugenol obtained in the prepn. of vanillin is best detd. by the m. p. of the mixt. of the benzoates, prepd. in C<sub>6</sub>H<sub>5</sub>N soln. The m. p. curve shows a eutectic point at 56.5°, corresponding to 25.5% isoeugenyl benzoate. At 83–86° and at compns. approx. the equimol. mixt., there is a discontinuity in the curve, probably due to the formation of a compd. which dissociates below its m. p. The following figures give the % of isoeugenyl benzoate and the m. p. of the mixt.: 0, 69.5°; 16, 64°; 29, 65.8°; 32, 69.4°; 35, 72.5°; 40, 79.7°; 46.5, 82.7°; 51.5, 83.6°; 54.9, 84°; 86.2°; 53.6, 86°; 59.68, 86.8°; 87.3, 91.4°; 98.0, 98.2°; 100, 104°.

C. J. WEST

**Relations between the configuration and the physical properties of esters of halogenated cinnamic acids.** K. V. AUWERS AND E. SCHMELLENKAMP. Marburg. *Ber.* 54B, 624–32(1921).—The present investigation was undertaken to det. whether the rule that for each pair of stereoisomeric cinnamic esters the stable form has a higher refractive and dispersive power is general and can be used, along with Stoermer's rule as to the b. ps. of the Me esters, to det. the configuration of any given ester. The halogenated cinnamic acids used were prepd. according to the directions of Stoermer and Heymann (*C. A.* 7, 2566) but for the prepn. of the esters (the Et instead of the Me esters were used) neither Et<sub>2</sub>SO<sub>4</sub> nor the Ag salts with EtI gave satisfactory results; they were, however, easily obtained with abs. EtOH and concd. H<sub>2</sub>SO<sub>4</sub>; why, with the same reagents, Barisch (*J. prakt. Chem.* 20, 184(1879)) found that the labile PhCH:CBrcO<sub>2</sub>H gave the stable acid and its ester, v. A. and S. are unable to explain. In every case the acid was boiled 2–3 hrs. with 5 parts abs. alc. and 0.5 part concd. H<sub>2</sub>SO<sub>4</sub> freed from alc. by distn., treated with H<sub>2</sub>O, taken up in Et<sub>2</sub>O, shaken with soda and with H<sub>2</sub>O, dried with CaCl<sub>2</sub>, evapd. and treated 0.5 hr. at 40–50° with dry air. Below are given, resp., the b. p.,  $d_4^{20}$ ,  $n$  for  $\alpha$ ,  $D$ ,  $\beta$  and  $\gamma$  at  $t^\circ$  and  $E_D$  for  $\alpha$ ,  $D$ ,  $\beta$  —  $\alpha$  and  $\gamma$  —  $\alpha$  (the last two in %) for the different halogenated cinnamic esters:  $\alpha$ -Cl (Et ester): trans,  $b_D$  188–90°, 1.1823, 1.59903, 1.57650, 1.59801, — at 13.4°, 1.56, 1.67, 63, —; cis,  $b_D$  169–70°, 1.1651, 1.54840, 1.55440, 1.57163, 1.58769 at 12.1°, 1.13, 1.19, 60, 68.  $\alpha$ -Br (Et ester): trans,  $b_D$  182–3.5, 1.4008, 1.58358, 1.59114, 1.61281, 1.63425, at 14.4°, 1.20, 1.30, 84, 96; cis,  $b_D$  175°, 1.5675, 1.56657, 1.57310, 1.59160, — at 12.7°, 1.20, 1.27, 63, —.  $\beta$ -Cl (Me ester): trans,  $b_D$  113–4°, 1.2248, 1.57119, 1.57810, 1.59791, 1.61671 at 21.4°, 1.16, 1.24, 69, 79; cis,  $b_D$  96–7°, 1.1932, 1.54878,



1.55457, 1.57094, 1.58566 at 26.5°, 0.97, 1.02, 47, 52.  $\beta$ -Br (Me ester): trans,  $b_{0.4}$  122°, 1.4520, 1.58636, 1.59338, 1.61319, 1.63175 at 20.2°, 1.04, 1.10, 61, 69; cis,  $b_{0.4}$  110-1°, 1.3836, 1.55560, 1.56124, 1.57886,—at 70.8°, 1.13, 1.17, 51, —.  $\beta$ -Br (Et ester): trans,  $b_{11}$  167°, 1.4044, 1.57749, 1.58405, 1.60278, 1.61990 at 10.1°, 0.94, 1.00, 59, 64; cis,  $b_{11}$  146°, 1.3818, 1.56190, 1.56761, 1.58393, 1.59886 at 10.1°, 0.79, 0.83, 43, 48.  $\alpha$ -I (Me ester): trans,  $b_{0.48}$  132-3°, 1.6679, 1.62427, 1.63298, 1.65783,—at 20.5°, 0.94, 1.01, 66, —.  $\alpha$ ,  $\beta$ -Cl<sub>2</sub> (Me ester): trans,  $b_{0.4}$  121°, 1.3053, 1.55640, 1.56202, 1.57762,—at 23°, 0.69, 0.73, 40, —; cis,  $b_{0.4}$  113°, 1.3042, 1.55871, 1.56445, 1.58055,—at 18.75°, 0.80, 0.84, 44,—.  $\alpha$ ,  $\beta$ -Br<sub>2</sub> (Me ester): trans,  $b_{0.4}$  138°, 1.6607, 1.56723, 1.57295, 1.58910,—at 75.0°, 0.67, 0.69, 37, —; cis,  $b_{0.4}$  124°, 1.7199, 1.59330, 1.59965, 1.61759,—at 20.6°, 0.70, 0.73, 43, —. A comparison of the above values with those for the *trans*- and *cis*-forms of PhCH:CHCO<sub>2</sub>Et and PhCMe:CHCO<sub>2</sub>Me, *trans*-PhCH:CMcCO<sub>2</sub>Et and *trans*-PhCMe:CMcCO<sub>2</sub>Et shows that Cl exerts about the same influence, both in the  $\alpha$ - and in the  $\beta$ -position, as Me as a disturbing substituent, in conformity with earlier observations;  $\beta$ -substituted derivs. of PhCH:CHCO<sub>2</sub>H, therefore, regularly have lower exaltations than the  $\alpha$ -derivs. The entrance of a Cl atom in the  $\alpha$ -position does not change the exaltation in the dispersive power of the stable or of the labile esters, although a decrease would be expected, but it has been frequently observed that the dispersion of optically exalted compds. is less influenced than the refraction by disturbing substituents. In general the halogens make their disturbing influence more strongly felt with increase in their at. wt. although this is shown strikingly only for I, for while the *trans*-Br compds. have somewhat smaller exaltations than the corresponding Cl compds. in the *cis*-esters these differences disappear and in fact are almost reversed. However, the  $E\lambda$  values of *cis*-PhCBr:CHCO<sub>2</sub>Me cannot be compared directly with those for the Cl compd., as the former were detd. at a higher temp. and by analogy about 0.2 must be subtracted from the values for the refraction. The entrance of 2 halogen atoms into the conjugated system exercises as strong an influence as the entrance of 2 Me groups; in the *cis*-compds. this is less well marked. The main question, as to whether the configuration of any given deriv. of PhCH:CHCO<sub>2</sub>H can be detd. from its specific exaltations, must be answered in the negative. While in the case of compds. previously examd. the exaltations of the *trans*-forms are regularly greater than those of the *cis*-derivs. this is usually but not always true for the halogenated esters. Likewise the *trans*-forms usually but not always have higher indexes of refraction. As regards densities the only case hitherto known in which the *trans*-form does not have a higher value is that of the two PhCH:CHCO<sub>2</sub>Et, for which Brühl found (*Z. physik. Chem.* 21, 392 (1896))  $d_4^{20}$  1.049 and 1.048 for the *trans*- and *cis*-forms, resp. Believing that his sample of the *allo*-ester, which had been prepd. by Liebermann from the Ag salt and EtI, might have been impure, v. A. and S. likewise prepd. it by L.'s method and obtained the following const., fully confirming B.'s observations.  $b_{11}$  125°,  $d_4^{11.4}$  1.1569,  $d_4^{20}$  1.049,  $n$  1.54110, 1.54833, 1.56598, 1.58243 for  $\alpha$ ,  $D$ ,  $\beta$  and  $\gamma$  at 11.4°,  $E\lambda$  1.27, 1.35, 62, 71 for  $\alpha$ ,  $D$ ,  $\beta$  —  $\alpha$  and  $\gamma$  —  $\alpha$ . The freshly prepd. *trans*-ester  $b_{11}$  158.5-9.0°,  $d_4^{11.4}$  1.0566. Hence, Stoermer's rule (b. p. of the Me esters) is the only one which thus far has been found to be without exception (19 cases) but the other const. are not without value in helping to det. configuration, for while they do not always follow the general rule, no case has yet been observed for any given pair of isomers in which more than two of these const. deviate from the normal in their relation to each other.

CHAS. A. ROUILLER

**4,7-Dihydroxycoumarin.** K. G. BAUER AND F. SCHODER. *Arch. Pharm.* 259, 53-9 (1921).—This work was undertaken for the purpose of detg. the applicability of Hoesch's reaction (cf. *C. A.* 9, 2541) to the esters of cyano fatty acids. It developed that NCCH<sub>2</sub>CO<sub>2</sub>Et condenses with resorcinol as expected, but that the ketimine of

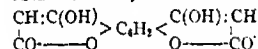


Et dihydroxybenzoylacetate cannot be isolated as such on account of the ease with which it suffers hydrolysis to the corresponding acid. The latter immediately loses

$\text{H}_2\text{O}$  and forms 4-imino-7-hydroxycoumarin,  $\text{HOC}_6\text{H}_3 < \begin{array}{c} \text{C}(\text{:NH})\text{CH}_2 \\ \text{O} \text{-----} \text{CO} \end{array}$ , from which 4,7-

dihydroxycoumarin is obtained. A soln. of  $\text{NCCH}_2\text{CO}_2\text{Et}$  and resorcinol in dry  $\text{Et}_2\text{O}$  treated with  $\text{ZnCl}_2$  and dry  $\text{HCl}$  at the ordinary temp. for 7 or 8 days yields 4-imino-7-hydroxycoumarin, pale red, microcryst. powder, m.  $311^\circ$  (decompn.). Boiling  $\text{NaOH}$  converts it into 4,7-dihydroxycoumarin, matted needles, m.  $264^\circ$  (decompn.), the constitution of which is seen in its conversion by  $\text{KOH}$  into 2,4-( $\text{HO}$ ) $_2\text{C}_6\text{H}_3\text{Ac}$ , m.  $143^\circ$   $\text{CH}_3\text{N}_2$  or  $\text{Me}_2\text{SO}_4$  changes 4,7-dihydroxycoumarin into 4,7-dimethoxycoumarin, needles, m.  $162^\circ$ , while  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  convert it into 4,7-diacetoxycoumarin, prisms, m.  $145.5^\circ$ . 4-Anilino-7-hydroxycoumarin,  $\text{HOC}_6\text{H}_3 < \begin{array}{c} \text{C}(\text{NHPh})\text{:CH} \\ \text{O} \text{-----} \text{CO} \end{array}$ , pale brown needles, m.  $176^\circ$ . Conc'd.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  change 4,7-dihydroxycoumarin into 6,8(?)

dinitro-4,7-dihydroxycoumarin, pale yellow needles, m.  $240\text{--}70^\circ$ . With  $\text{Br}$  in  $\text{CCl}_4$  8(?)-bromo-4,7-dihydroxycoumarin is formed, pale yellow leaflets, m.  $127^\circ$ . Reduction of 4,7-dihydroxycoumarin with  $\text{Zn}$  and  $\text{HCl}$ , or  $\text{Zn}$  dust and glacial  $\text{AcOH}$ , yields in the presence of alc. 7-hydroxydihydrocoumarin, needles, m.  $252^\circ$  (decompn.) after darkening at  $210^\circ$ . In treating resorcinol with 2 mols. of  $\text{NCCH}_2\text{CO}_2\text{Et}$  a product was obtained which yielded with  $\text{NaOH}$  a substance,  $\text{C}_{12}\text{H}_8\text{O}_6$ , possibly formulated as follows:



W. O. E.

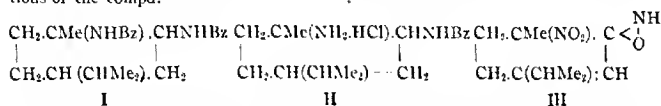
**The hemiterpenes.** ANDRÉ DUBOSC. *Rev. prod. chim.* 24, 273-6, 307-10, 371-5 (1921)—General review of the chemistry of the hemiterpenes and especially of isoprene.

A. P.-C.

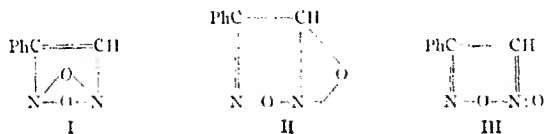
**Addition reactions with nitrogen oxides.** HEINRICH WIELAND. **Introduction.** *Ann.* 424, 71-4 (1921); cf. *Ann.* 328, 154; 329, 225; 340, 63. I. The addition of  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  to unsaturated compounds. HEINRICH WIELAND and EWALD BLUMICH. *Ibid* 75-91.—*Stilbene pseudonitrosite*,  $(\text{O}_2\text{NCHPhCHPh})_2\text{N}_2\text{O}_3$  prep'd. by passing  $\text{NO}$ -rich gases (from  $\text{As}$  and  $\text{HNO}_3$ , d. 1.23) into 10 g. stilbene in 350 cc.  $\text{Et}_2\text{O}$ , for 2-3 hrs., and extg. the product with about 40 cc.  $\text{Me}_2\text{CO}$ , fine needles, m.  $132^\circ$ . It gives the Liebermann reaction with  $\text{PhOH}$  and  $\text{H}_2\text{SO}_4$ . Boiling alc. decomp. it into stilbene and  $\text{N}_2\text{O}_4$ . Boiled with  $\text{AcOH}$ , it decomp. into stilbene and  $\text{N}_2\text{O}_3$ , in part and in part into a mixt. of equal parts of  $\alpha$ - and  $\beta$ - $\text{Ph}_2\text{C}_2\text{H}_2(\text{NO}_2)_2$ . Besides this reaction, a 2nd occurs, in which  $\text{H}_2\text{O}$  reacts with the pseudonitrosite to form  $\text{BzH}$ ,  $\text{PhCH}_2\text{NO}_2$  and  $\text{N}_2\text{O}$ . With alc.  $\text{KOH}$ ,  $\alpha$ -nitrostilbene (*Ber.* 37, 4509) is formed. *Phenylbromonitromethane*,  $\text{C}_7\text{H}_5\text{BrO}_2\text{N}$ , was prep'd. by adding 500 cc. sat'd.  $\text{Br-H}_2\text{O}$  with 22.7 g. *aci-PhCH}\_2\text{NO}\_2\text{Na}, pale yellow oil,  $b_{19}$   $122^\circ$ ,  $b_{16}$   $131^\circ$ . A by-product is  $\alpha,\beta,\gamma$ -triphenylisoxazole (C. A. 5, 3270). Shaken with mol.  $\text{Ag}$ , about 13% of diphenyldinitroethane is formed, needles, m.  $225^\circ$ . *Cyclohexene pseudonitrosite*,  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$ , (Baeyer, *Ann.* 278, 110), needles, m.  $145^\circ$ .  $\text{MeOH-KOH}$  decomp. it into  $\text{H}_4\text{O}_2\text{N}_2$  and nitrocyclohexene,  $\text{C}_6\text{H}_9\text{O}_2\text{N}$ , pale yellow oil,  $b_{14}$   $100^\circ$ . Reduction with  $\text{Zn}$  dust in 90%  $\text{AcOH}$  gave  $\text{NH}_3$  and cyclohexanone oxime (besides cyclohexanone). The action of  $\text{NO}$  upon  $\text{C}_{10}\text{H}_{16}$  in a mixt. of  $\text{C}_6\text{H}_6$  and gasoline gave principally  $\text{C}_{10}\text{H}_{18}$ , with  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{NO}_3$  as a by-product. A pure pseudonitrosite was not isolated. The action of  $\text{NO}_2$  upon dibenzalacetone gives a dinitrite,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$ , decomp.  $127\text{--}9^\circ$ . The yield is small.  $\text{MeOH-NH}_3$  decomp. it into  $\text{BzH}$  and  $\text{PhCH:CHCOCH}_2\text{NO}_2$  (Harries, *Ann.* 319, 254), besides  $\text{NH}_4\text{NO}_3$ . The action of  $\text{MeOH-KOH}$  leads to another decompn., in which  $\text{PhCH:CHNO}_2$ ,  $\text{PhCH:CHCO}_2\text{H}$  and  $\text{NH}_4\text{NO}_3$  are formed. II. Nitrosites of the terpenes. HEINRICH WIELAND and FRITZ REINDEL. *Ibid* 92-9.—In an*



attempt to det. the structure of terpinene nitrosite, the product was reduced in Et<sub>2</sub>O suspension by H<sub>2</sub>, with Pd black as catalyzer. During the reduction about 25% of the N was split off as NH<sub>3</sub>. The reduced product was shaken out of the Et<sub>2</sub>O with HCl, but the products (a mixt. of a monoamine and a diamine) could not be sepd. by fractional distn. Treated with BzCl, two products were obtained; *Dibenzoyl-1,2-diaminophexahydrocymene* (I), fine needles from alc., m. 165°. A second product obtained by extg. the base with HCl and treating with BzCl, proved to be the *hydrochloride of the monobenzoyl derivative* (II), fine needles, m. 290°. The constitution of the nitrosite is, therefore, probably (III). W. and R. believe this explains all the reactions of the compd.



III. Addition of the higher nitrogen oxides to the triple carbon linking. HEINRICH WIELAND AND EWALD BLÖMICH. *Ibid* 100-6.—The addition of N<sub>2</sub>O<sub>4</sub> to 3 g. PhC≡CH in a mixt. of Et<sub>2</sub>O and gasoline till the gain in wt. was 4 g., gave 1.5 to 2 g. *phenyldinitroethylene*, PhC(NO<sub>2</sub>):CHNO<sub>2</sub>, large, golden yellow needles, m. 81°, decomp. about 100°. Concd. H<sub>2</sub>SO<sub>4</sub> gives a brown soln., from which H<sub>2</sub>O ppts. the compd. unchanged. Alkali decomp. the product into PhCN, carbonate and nitrite. The work of Schmidt on the addition of N<sub>2</sub>O<sub>4</sub> to toluene is confirmed (*Ber.* 34, 620); the red by-product is a *dinitrodiphenylacetylene*, C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub>, m. 234°. Even when the dinitrostilbenes are reduced by H<sub>2</sub> and Pd, part of the N is split off as NH<sub>3</sub>. One of the products of the reduction is desoxybenzoin oxime, m. 98°. The action of alc. KOH upon the dinitrostilbenes leads to the formation of *α-nitro-β-methoxystilbene*, C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N, sepd. by soln. in MeOH, yellow prisms, m. 88-9°, and *α-nitrodesoxybenzoin acetal*, C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>N, long needles, m. 202-3°. IV. The constitution of furoxan (glyoxime peroxide). HEINRICH WIELAND. *Ibid* 107-16.—W. discusses Green's formulation (*C. A.* 7, 1353, 3119), and defends his own (*C. I.* 4, 3199; 3, 2635). PhC≡CH and N<sub>2</sub>O<sub>4</sub> give a phenylfuroxan, which m. 108° (decomp.). Recrystd. from MeOH, Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>6</sub>-gasoline, it m. 80-7° (Schödl, *Ber.* 23, 3504). The higher melting form is also formed as the 1st product of the oxidation of phenylglyoxime with N<sub>2</sub>O. The chem. identity of the 2 is shown by their transformation by Na<sub>2</sub>CO<sub>3</sub> into phenoxylurazan. The labile isomer may have the structure of an intramol. bisnitroso compd. (D), in the sense used by Green:



They may also represent an isomerism between II and III. These 2 formulas are different expressions for the same compd. C. J. WIER

Influence of constitution upon the rotatory power of optically active organic compounds. H. RUBE XIII. The absorption spectra of several optically active compounds. ALFRED KRETHLOW AND KARL LANGBEIN. *Univ. Basel. Ann.* 423, 321-43 (1921); cf. *C. A.* 15, 591. The investigation of 33 substances shows that there is apparently no parallelism between anomalous rotation dispersion and the selective spectral absorption of a compd. In only 3 of the compds. examd. was there positive evidence of anomaly of the rotation dispersion with selective light absorption. Of



these, 2 were colorless (menthyl diphenylmethyloacetate, and menthyl phenylbenzoylacetate) and only 1 is pale yellow (diphenylmethylenecamphor). It is doubtful whether Cotton's phenomenon is present in these cases, for even with these compds. there is hardly a true selective absorption but simply the beginning, for the curve is continuous and simply shows a flattening between 344 and 410  $\mu$ . The results are shown in curves.

C. J. West

**Piperitone. I. The occurrence, isolation and characterization of piperitone.** JOHN READ AND HENRY GEORGE SMITH. Univ. Sydney. *J. Chem. Soc.* 119, 779-89 (1921); cf. Smith and Penfold, *C. A.* 15, 572.—Piperitone occurs in largest amts. in the oil of *Eucalyptus dives*, "broad-leaved peppermint." The yield of oil from the green leaves and twigs amounts to as much as 4% and when the distn. is continued for about 8 hrs., the resulting oil may contain up to 40% of piperitone. Cineole is not an abundant constituent of oils containing piperitone. Piperitone is isolated by fractional distn. at atm. pressure, followed by treatment with  $\text{NaHSO}_4$ . *dl*-Piperitone hydroxylamino-oxime,  $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$ , small needles from EtOH containing a little  $\text{Et}_2\text{O}$ , m. 169-70°. It reduced Fehling soln. and gave a blue color when boiled in alc. with  $\text{HgO}$ . A soln. in alc.- $\text{CHCl}_3$  gave a bright bluish green color with a trace of Br, changing to emerald-green upon the addition of more Br. If exactly 1 mol.  $\text{NH}_4\text{OH}$  is used, the oxime results,  $\text{C}_{10}\text{H}_{17}\text{ON}$ , prisms from light petroleum, m. 110-1°. *Semicarbazone*,  $\text{C}_{10}\text{H}_{15}\text{ON}_3$ , minute crystals, m. 219-20°. *Benzylidene-dl*-piperitone,  $\text{C}_{10}\text{H}_{14}\text{O}$ : $\text{CHPh}$ , by adding 1 g. Na in 50 cc. EtOH to 25 g. piperitone and 17.5 g.  $\text{BzH}$  in 60 cc. alc., neutralizing with  $\text{H}_2\text{SO}_4$  after 3-4 days and extg. with  $\text{Et}_2\text{O}$ , pale yellow prisms from MeOH or EtOH with pronounced luster and transparency, m. 61°,  $n_D^{25}$  1.45-58°,  $n_D^{100}$ ,  $b(10)$ ,  $c(001)$ ,  $m(110)$ ;  $a:b:c::0.9331:1:—$ .  $\beta = 72^\circ 36'$ . A 15%  $\text{HBr}$ -AcOH soln. gave a dark red soln. but the compd. is pptd. unchanged after several hrs. by  $\text{H}_2\text{O}$ . With  $\text{NH}_4\text{OH}$ , *benzylidene-dl*-piperitone oxime results,  $\text{HON}:\text{C}_{10}\text{H}_{14}:\text{CHPh} \cdot \text{H}_2\text{O}$ , rosetts of small needles from MeOH, softens 89°, m. 130-1.5°.

C. J. West

**Camphane series. XXXIX. *p*-Aminophenylaminocamphor (camphoryl-*p*-phenylenediamine).** MARTIN ONSLOW FORSTER AND WILLIAM BRISTOW SAVILLE. Royal Institution. *J. Chem. Soc.* 119, 789-98 (1921); cf. *C. A.* 14, 2915.—Phenylaminocamphor (A) develops a characteristic intense cherry-red color with concd.  $\text{HNO}_3$ , which fades to a pale brown in a few hrs. *Hydrochloride*,  $\text{C}_{16}\text{H}_{21}\text{ON} \cdot \text{HCl}$ , decomp. 199°. *Acetate*,  $\text{C}_{16}\text{H}_{21}\text{O}_2\text{N}$ , m. 104°,  $[\alpha]_D -35.3^\circ$ . *Dinitro derivative*,  $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}_2$ , by adding 10 cc.  $\text{HNO}_3$  to 5 g. A in 10 cc. AcOH, with a color change from purple through green to brown, orange crystals, m. 191° (from alc.), 204° (from  $\text{Me}_2\text{CO}$ ),  $[\alpha]_D -120.7^\circ$ . Phenylnitrosoaminocamphor (B) (*C. A.* 3, 2801), needles, m. 74° (not 80-1°),  $[\alpha]_D$  changes from  $-3.6^\circ$  to  $6.5^\circ$  in 2 hrs. *N*-Phenylcamphorimide oxime,  $\text{C}_{16}\text{H}_{19}\text{C}(\text{NOH})-$

$\text{NPhCO}$ , by adding 5 g. B in small portions to 1.3 g. KOH in 2 g.  $\text{H}_2\text{O}$  and 8 cc. alc.;

diln. with 40 cc.  $\text{H}_2\text{O}$  pptd. 0.4 g. phenyliminocamphor, and neutralizing with AcOH gave the oxime, minute, thread-like needles, m. 135°,  $[\alpha]_D 247.6^\circ$ . The alc. soln. gives an intense red color with  $\text{FeCl}_3$ . Boiled with HCl for 2 hrs., camphoric acid is formed, besides  $\text{PhNH}_2$  and  $\text{NH}_4\text{OH}$ . *Benzate*, m. 177°,  $[\alpha]_D 122.4^\circ$ . When 20 g. B in 70 cc. glacial AcOH is treated with a mixt. of 7 g. 70%  $\text{HNO}_3$  and 10 cc. glacial AcOH, and the product extd. with light petroleum, the residue is *p*-nitrophenylnitrosoaminocamphor (C),  $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_2$ , pale straw-colored needles from  $\text{Me}_2\text{CO}$ , decomp. 158°,  $[\alpha]_D 35^\circ$ . The *o*-derivative (D) is found in the ext., minute, transparent straw-colored prisms, decomp. 122°,  $[\alpha]_D 114.9^\circ$ . Mixts. m. between 129° and 158°. The *o*-compd. may be extd. from such mixts. by extg. with cold  $\text{C}_6\text{H}_6$  and pptg. the more



sol. isomer with an equal vol. of cold petroleum. Reduced with Na in alc.; C gives *p*-nitrophenyliminocamphor,  $C_{16}H_{15}O_2N_2$ , yellow crystals, m.  $136^\circ$ ,  $[\alpha]_D^{25}$   $372.4^\circ$ . *o*-Derivative, lustrous yellow plates, m.  $142^\circ$ ,  $[\alpha]_D^{25}$   $109.4^\circ$ . A mixt. of the 2 in equal parts m.  $122^\circ$ , and is not changed by crystn. from alc. The *p*-deriv. is readily hydrolyzed by AcOH, the *o*-deriv. less readily. *p*-Acetylaminophenylaminocamphor,  $C_{18}H_{19}O_2N_2$ , is prepd. by reducing the imino deriv. with Zn dust, m.  $167^\circ$ ,  $[\alpha]_D^{25}$   $87.5^\circ$ . On heating 20 g. with 100 cc. alc. and 100 cc. concd. HCl for 3 hrs., *p*-aminophenylaminocamphor dihydrochloride,  $C_{16}H_{17}ON_2 \cdot 2HCl$ , is obtained as lustrous needles, decomp.  $190^\circ$ . The free base (E), pale brown crystals, m.  $106^\circ$ ,  $[\alpha]_D^{25}$   $95.1^\circ$ . Benzoate, m.  $206^\circ$ . Camphorylaminophenyliminocamphor,  $C_{26}H_{27}O_2N_2$ , from E and camphorquinone in alc., dense, spherical nodules, m.  $234^\circ$ ,  $[\alpha]_D^{25}$  in  $CHCl_3$   $1641^\circ$ , in  $C_6H_5N$   $1990^\circ$ ; therefore,  $[M]_D^{25}$   $6663^\circ$  and  $8079^\circ$ . *p*-Nitrobenzenesazophenylaminocamphor,  $C_{22}H_{21}O_2N_4$ , from *p*- $O_2NC_6H_4N_2Cl$  and A, vermilion leaflets with gold reflex, m.  $207-8^\circ$ ; dark red prisms sep. from  $Me_2CO$ . *p*-Sulfobenzenesazophenylaminocamphor,  $C_{22}H_{21}O_2N_4S$ , deep red needles which become purple in sunlight, intumescence at  $235^\circ$ . It crysts. with 1 EtOH; a portion indissolved after continued treatment with boiling water is dark purple, intumescence  $263^\circ$ . The dry substance has a sternutatory effect. The alc. soln. gives an intense carmine color with HCl. *p*,*p*-Diphenylenebisazophenylaminocamphor,  $C_{24}H_{23}O_2N_4$ , brown, m.  $241^\circ$ . Alc. HCl gives an intense blue color. *p*-Sulfobenzenesazophenylaminocamphor,  $C_{22}H_{21}O_2N_4S$ , dark green crystals, which contain 1.5 AcOH, m.  $213^\circ$ . Rubbed on glass, the green crystals leave a violet stain. 4-Amino-1-naphthylaminocamphor (camphoryl-1,4-naphthylenediamine),  $C_{20}H_{19}ON_2$ , by reducing the azo compd. with dil. alc. KOH, isolated as the hydrochloride, hard nodules. Camphoryl-1-aminonaphthyl-4-iminocamphor, brick-red, m.  $195^\circ$ ,  $[\alpha]_D^{25}$  in  $CHCl_3$   $1680^\circ$ , in  $C_6H_5N$   $2031^\circ$ ; therefore,  $[M]_D^{25}$   $7688^\circ$  and  $9261^\circ$ . C. J. WASSER

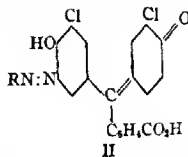
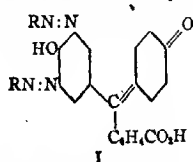
Some nitronic derivatives. L. ALESSANDRI. R. Ist. Studi Sup. Florence. *Gazz. chim. ital.* 51, 1, 75-89 (1921).—Owing to the recent publications by Semper and Lichtenstadt (C. A. 13, 590) and by Standinger and Miescher (C. A. 14, 1971) involving in part the nitronic derivs. obtained by Angeli, Mancini and Alessandri (C. A. 5, 3403) and by Alessandri (C. A. 9, 1045), A. is now publishing additional results. S. and L. confirmed and extended A.'s results by finding 4 isomers for  $MeC_6H_4C_6H_4NOH$ . They failed to observe that the *O*-Me deriv.,  $PhC:N:OMe$ , heated in the air in an open test-tube at the m. p., decomp. violently, giving a luminous flame, but is not decompd. by prolonged exposure to light; the *N*-Me deriv. is easily decompd. by light. This influence of light on the *N*-derivs. was fully studied by Angeli, A. and Pegna (C. A. 4, 2457) and by A. (C. A. 4, 276). After completing his military service A. extended the study of the influence of heat. He found that the *N*-Ph deriv.,  $PhCH:N(O)Ph$  heated as the *O*-deriv. above undergoes an analogous decomposition, giving a luminous flame and an oily residue from which  $BzNHPh$  crystals. The corresponding derivs. of anisaloxime and saicylaloxime behave similarly and give the corresponding anilides. These and other results had been obtained when S. and M.'s paper appeared giving these results, but in which they had overlooked A.'s former results. The earlier work on the hydroxylamines and the nitrones derived from it by oxidation, in which it was found that  $Ph_2CH.N(OH)Ph$  gives a product with 2 H atoms less, which Staudinger has alleged to be the *N*-Ph deriv. of benzophenone oxime (A) (diphenyl-*N*-phenylnitron),  $Ph_2C:N(O)Ph$ , was then extended. If this is the constitution of the above product then it should give  $Ph_2CO$  and  $PhNO$  on oxidation with  $CrO_2$  and  $Ph_2CHNHPh$  on reduction with  $Al-Hg$ , but this was not successful. Reduction of  $PhCH:N(O)Ph$  with  $Zn + NH_4Cl$  gives  $PhCH:NPh$  and A. to behave similarly should give  $Ph_2C:NPh$  (B), m.  $116^\circ$ . Instead of this A. actually gave a compd. (C) m.  $83^\circ$ . Assuming that C is a mol. addition compd.



between B and another product of further reduction (benzohydrylphenylamine (D)) A. prepd. B and D and on crystg. them together obtained the compd. C. From this it is concluded that S.'s formula for A is satisfactory and that this on reduction with Zn + NH<sub>4</sub>Cl gives the addition product just described by the mol. addition of 2 stages in the reduction. C represents a new type of addition compd. for these compds. A. has now shown that the product previously obtained (C. A. 9, 1045) on oxidizing PhCHN(OH)CH<sub>2</sub>Ph is Ph<sub>2</sub>CHN(:O):CHPh (E). In prepg. a quantity of E the Ph<sub>2</sub>C:N(:O)CH<sub>2</sub>Ph was found in the mother liquors. It was previously found that E on treatment with EtMgI gave an orange-yellow oil, which did not cryst. Suspecting that this was due to the greater oxidizing power of EtMgI A. used PhMgBr instead and obtained a yellowish oil from which the expected (Ph<sub>2</sub>CH)<sub>2</sub>NOH (F) did not cryst. but Ph<sub>2</sub>C:N(:O)CHPh<sub>2</sub> (G) instead. Hydrolysis of F with HCl did not give results significant for the constitution but reduction with Hg-Al readily gave the known (Ph<sub>2</sub>CH)<sub>2</sub>NH. That G is really formed by the oxidation of the main reaction product was shown by oxidizing the orange oil remaining with HgO by which much more E was obtained. For reasons given A. believes that the orange oil is Ph<sub>2</sub>CHN(:O)CHPh<sub>2</sub> and that for this reason F could not be obtained cryst. Other expts. at lower temps. with other oxidizing agents and reagents may permit A. to isolate and identify some of these intermediate compds. and complete the study of these reactions. Finely powdered A was suspended in much Et<sub>2</sub>O and treated with an equal wt. of NH<sub>4</sub>Cl in H<sub>2</sub>O. To this small amts. of Zn dust were added with agitation. The mixt. was cooled under the tap it became warm and finally the Et<sub>2</sub>O soln. was sepd. and on evapn. deposited crystals of C. 5 g. of PhCH:N(:O)CH<sub>2</sub>Ph, m. 82°, treated with 1 mol. PhMgBr, by the method previously described (C. A. 5, 3403), gave on evapg. the Et<sub>2</sub>O containing the benzohydryl-β-hydroxylamine, m. 105°, a gray residue which in CHCl<sub>3</sub> was treated with HgO in such an amt. as left a little excess even after heating a while on the H<sub>2</sub>O bath. The filtrate freed from solvents gave a residue from which 2.6 g. PhCH:N(:O)CHPh<sub>2</sub> (H), m. 159°, crystd. Two g. finely powdered dry H were nearly dissolved in abs. Et<sub>2</sub>O under a condenser and the soln. was treated rapidly with 0.25 g. Mg in an Et<sub>2</sub>O soln. of 1.64 g. PhBr. The mixt. was boiled on the H<sub>2</sub>O bath. The next day H<sub>2</sub>O was gradually added and the flocks sepd. were taken up in Et<sub>2</sub>O and G was finally sepd. as colorless refractive crystals, m. 163–4°. Details concerning the reduction of G and the oxidation of the yellow oil are also given.

E. J. WITZEMANN

The constitution of phenolphthalein. F. CONSONNO and C. APOSTOLO. R. Polytecnico, Turin. *Gazz. chim. ital.* 51, I, 50–4(1921).—There is still discussion as to whether a benzenoid or quinonoid structure should be assigned to phenolphthalein (A). Baeyer decided for the benzenoid form in 1880 but Oddo reinvestigated it by detg. the behavior of A on copulation with diazonium compds. at 0°. From this work since azoic groups were introduced O. confirmed B.'s formula but pointed out that it was barely possible that the 2 azoic groups entered into 1 nucleus in the quinonoid form as in I. C. and A. wished to find conditions under which the formation of I would be impossible and selected dichlorophenolphthalein (B) for this purpose, which was ob-



tained by condensing *o*-ClC<sub>6</sub>H<sub>4</sub>OH with phthalic anhydride: straw-colored solid, m.



98°. B condensed with  $p\text{-MeC}_6\text{H}_4\text{N}_2\text{Cl}$  gave  $p\text{-tolylazodichlorophenolphthalein}$  (II). The result of this copulation shows that phenolphthalein and its salts have the quinonoid formula.

E. J. WITZEMANN

Use of aluminium chloride and ferric chloride in the preparation of phenolphthalein. CHARLES FREDERICK WARD. Univ. Coll., Nottingham. *J. Chem. Soc.* 119, 850-2 (1921).—Anhydrous  $\text{AlCl}_3$  gives an improved yield of phenolphthalein when the  $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  and  $\text{AlCl}_3$  are in mol. proportions and the  $\text{PhOH}$  is in slight excess. The product is clean and easily purified. Anhydrous  $\text{FeCl}_3$  is not so satisfactory, the yields being poor and the product more difficult to purify.  $\text{Ac}_2\text{O}$  has no action as a condensing agent in this reaction. Since  $\text{ZnCl}_2$  gives a better yield than  $\text{AlCl}_3$  (*C. A.* 15, 1966) this work was discontinued.

C. J. WEST

Synthesis of mono- or dihasic acids by the action of malonic acid on substituted benzohydrols. LEON BAILLON. *Ann. chim.* 15, 61-108 (1921).—By heating 10 g. of  $(p\text{-MeOC}_6\text{H}_4)\text{CHPhOH}$  with 12 g. of  $\text{CH}_2(\text{CO}_2\text{H})_2$  on the water bath for 2 hours, extg. with warm  $\text{NaOH}$ , filtering and acidifying, 12 g. of  $p\text{-methoxy-}\beta,\beta\text{-diphenyl-isosuccinic acid}$  are obtained, white needles from boiling  $\text{H}_2\text{O}$ , easily sol. in  $\text{EtOH}$ ,  $\text{C}_6\text{H}_6$  and  $\text{Et}_2\text{O}$ , almost insol. in petr. ether, becoming opaque at  $100-5^\circ$ , m.  $178^\circ$  (decompn.). *Silver salt*, white flocks; *sodium salt*, white microneedles from dil.  $\text{EtOH}$ ; *calcium salt*, brilliant white crystals, slightly sol. in boiling  $\text{H}_2\text{O}$ ; *barium salt*, white microcrystals slightly sol. in boiling  $\text{H}_2\text{O}$ ; *magnesium salt*; *lead salt*, almost insol. in boiling  $\text{H}_2\text{O}$ . On heating for 15 mins. to  $180-200^\circ$ , the acid loses  $\text{CO}_2$  and forms  $(p\text{-MeOC}_6\text{H}_4)\text{CHPhCH}_2\text{CO}_2\text{H}$  (Fosse, *Compt. rend.* 1905, 614), insol. in petr. ether, sol. in  $\text{EtOH}$ , white prisms from a mixt. of petr. ether and  $\text{C}_6\text{H}_6$ , m.  $123-5^\circ$ ; *silver salt*. Equal parts of  $(p\text{-MeOC}_6\text{H}_4)(o\text{-MeC}_6\text{H}_4)\text{CHOH}$  and  $\text{CH}_2(\text{CO}_2\text{H})_2$ ; heated on the water bath for 1.5 hrs. give, after soln. in  $\text{NaOH}$ , acidifying, and recrystg. from  $\text{C}_6\text{H}_6$  with a little  $\text{EtOH}$ , small white crystals of  $p\text{-methoxy-}\beta,\beta\text{-phenyl-}o\text{-tolylisosuccinic acid}$ , m.  $191^\circ$  (decompn.). *Salts*: *silver*, white flocks; *sodium*, brilliant white crystals; *calcium*, *barium*, small white crystals; *magnesium*, brilliant needles; *lead*. By heating this acid to  $180-210^\circ$ , or by heating the reaction mixt. to  $150-80^\circ$ ,  $\text{CO}_2$  is evolved and  $p\text{-methoxy-}\beta,\beta\text{-phenyl-}o\text{-tolylpropionic acid}$  is formed, large colorless crystals from  $\text{C}_6\text{H}_6$  and petr. ether, m.  $101-2^\circ$ ; *silver salt*, white flocculent ppt. Similarly,  $p\text{-methoxy-}\beta,\beta\text{-phenyl-}p\text{-tolylisosuccinic acid}$ , sol. in  $\text{Et}_2\text{O}$  and warm  $\text{EtOH}$ , insol. in petr. ether, very small white needles from hot  $\text{EtOH}$ , m.  $195^\circ$  (loss of  $\text{CO}_2$ ). *Salts*: *silver*, pulverulent white ppt.; *sodium*; *calcium*; *barium*, white cryst. ppt.; *magnesium*, fine brilliant needles; *lead*; white flocks, almost insol. in  $\text{H}_2\text{O}$ . By heating the reaction mixt. to  $160-98^\circ$ , or by heating the acid to  $180-210^\circ$ ,  $\text{CO}_2$  is evolved and  $p\text{-methoxy-}\beta,\beta\text{-phenyl-}p\text{-tolylpropionic acid}$  is formed, sol. in  $\text{EtOH}$  and  $\text{C}_6\text{H}_6$ , insol. in petr. ether, transparent needles, m.  $140-2^\circ$ ; *silver salt*, gelatinous ppt. collecting into white flocks.  $p\text{-Methoxy-}\beta,\beta\text{-phenyl-}\alpha\text{-naphthylisosuccinic acid}$ , sol. in  $\text{EtOH}$  and  $\text{Et}_2\text{O}$ , slightly sol. in  $\text{C}_6\text{H}_6$  and petr. ether, white prisms, m. about  $100^\circ$ , solidifies, loses  $\text{CO}_2$  and m. again  $146^\circ$ . Heated to const. wt. at  $95^\circ$ , the crystals become opaque and m.  $146^\circ$ . *Salts*: *silver*, white flocculent ppt.; *sodium*, silvery leaflets; *calcium*; *barium*; *magnesium*, white needles; *lead*. On heating the above acid to  $180^\circ$ ,  $\text{CO}_2$  is evolved and  $p\text{-methoxy-}\beta,\beta\text{-phenyl-}\alpha\text{-naphthylpropionic acid}$  is formed, sol. in  $\text{EtOH}$  and  $\text{C}_6\text{H}_6$ , white needles, m.  $116-7^\circ$ ; *silver salt*, white flocculent ppt. The following acids were prepd. by the action of  $\text{CH}_2(\text{CO}_2\text{H})_2$  on 3,4-dimethoxybenzohydrols: 3,4-dimethoxy- $\beta,\beta\text{-diphenylisosuccinic acid}$ , very sol. in  $\text{Et}_2\text{O}$  and  $\text{EtOH}$ , slightly sol. in  $\text{C}_6\text{H}_6$ , insol. in petr. ether, brilliant white crystals, m.  $165^\circ$  and loses  $\text{CO}_2$ . *Salts*: *silver*, white ppt. turning to reddish brown in the light; *sodium*, brilliant crystals; *calcium*; *barium*; *magnesium*, white crystals; *lead*. Heating to  $160-80^\circ$  gives 3,4-dimethoxy- $\beta,\beta\text{-diphenylpropionic acid}$ , sol. in  $\text{EtOH}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{Et}_2\text{O}$ , slightly sol. in petr. ether, m. after drying  $109-11^\circ$ . *Silver salt*, white flocculent



ppt. 3,4-Dimethoxy- $\beta,\beta$ -phenyl-*o*-tolylisossuccinic acid, very sol. in EtOH, slightly sol. in Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub> and petr. ether, small white crystals, m. 177° with loss of CO<sub>2</sub>. *Salts*: silver, white flocculent ppt.; sodium; calcium; magnesium, white crystals; barium; lead, white flocculent ppt. 3,4-Dimethoxy- $\beta,\beta$ -phenyl-*o*-tolylpropionic acid, from the above acid by heating to 180–200°, large colorless prisms from C<sub>6</sub>H<sub>6</sub> and petr. ether, sol. in EtOH, m. 113–4°; silver salt. 3,4-Dimethoxy- $\beta,\beta$ -phenyl-*p*-tolylisossuccinic acid, sol. in EtOH and Et<sub>2</sub>O, almost insol. in petr. ether, silky needles, m. 185° with loss of CO<sub>2</sub>; silver, white flocculent ppt. soon changing to brown in the light; the acid on heating to 190–200° loses CO<sub>2</sub> and forms 3,4-dimethoxy- $\beta,\beta$ -phenyl-*p*-tolylpropionic acid, sol. in EtOH and C<sub>6</sub>H<sub>6</sub>, insol. in petr. ether, silky white needles, m. 135–6°. 3,4-Dimethoxy- $\beta,\beta$ -phenyl- $\alpha$ -naphthylisossuccinic acid, very sol. in EtOH and Et<sub>2</sub>O, very slightly sol. in C<sub>6</sub>H<sub>6</sub> and petr. ether, white silky needles, m. 144° with loss of CO<sub>2</sub>, forming 3,4-dimethoxy- $\beta,\beta$ -phenyl- $\alpha$ -naphthylpropionic acid, sol. in EtOH and C<sub>6</sub>H<sub>6</sub>, colorless crystals, m. 147–8°. The following acids were prepd. from 3,4-methylenedioxybenzohydrolyds: 3,4-methylenedioxy- $\beta,\beta$ -diphenylisossuccinic acid, difficultly sol. in C<sub>6</sub>H<sub>6</sub> and petr. ether, slightly sol. in hot H<sub>2</sub>O and easily sol. in Et<sub>2</sub>O and EtOH, small white needles from dil. EtOH, m. 141° with loss of CO<sub>2</sub>, forming 3,4-methylenedioxy-diphenylpropionic acid, easily sol. in C<sub>6</sub>H<sub>6</sub> and warm EtOH, slightly sol. in Et<sub>2</sub>O, brilliant needles, m. 155–6°; silver salt, white flocculent ppt. 3,4-Methylenedioxy- $\beta,\beta$ -phenyl-*o*-tolylisossuccinic acid, very sol. in EtOH and Et<sub>2</sub>O, difficultly sol. in C<sub>6</sub>H<sub>6</sub>, almost insol. in petr. ether, white crystals, m. 183° with loss of CO<sub>2</sub>, forming 3,4-methylenedioxy- $\beta,\beta$ -phenyl-*o*-tolylpropionic acid, sol. in EtOH and C<sub>6</sub>H<sub>6</sub>, slightly sol. in Et<sub>2</sub>O and petr. ether, brilliant prisms, m. 138° after drying for 1 hr. at 100°, then solidifies and m. 145–7°. 3,4-Methylenedioxy- $\beta,\beta$ -phenyl-*p*-tolylisossuccinic acid, very sol. in Et<sub>2</sub>O and EtOH, difficultly sol. in C<sub>6</sub>H<sub>6</sub> and petroleum ether, needles, m. 180° with loss of CO<sub>2</sub>, giving 3,4-methylenedioxy- $\beta,\beta$ -phenyl-*p*-tolylpropionic acid, m. 161° (Fosse, loc. cit.). 3,4-Methylenedioxy- $\beta,\beta$ -phenyl- $\alpha$ -naphthylisossuccinic acid, difficultly sol. in C<sub>6</sub>H<sub>6</sub> and petr. ether, white crystals from hot C<sub>6</sub>H<sub>6</sub> with a few drops of AcOH, m. 185° with loss of CO<sub>2</sub>, and resolidifies, m. again 205–6°, which is the m. p. of 3,4-methylenedioxy- $\beta,\beta$ -phenyl- $\alpha$ -naphthylpropionic acid, slightly sol. in EtOH, Et<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>, small white needles. Silver salt, white flocks. The following acids were derived from *p*-dimethylaminobenzohydrolyds: *p*-dimethylamino- $\beta,\beta$ -diphenylisossuccinic acid, slightly sol. in C<sub>6</sub>H<sub>6</sub>, petr. ether, Et<sub>2</sub>O and cold EtOH, more sol. in boiling EtOH, white needles, m. 124°, forming a pasty mass which evolves CO<sub>2</sub> and solidifies; silver salt, white flocks becoming brown in the light. *p*-Dimethylamino- $\beta,\beta$ -diphenylpropionic acid, by heating the above acid to 150–70°, brilliant white needles, slightly sol. in Et<sub>2</sub>O, rather sol. in EtOH and warm C<sub>6</sub>H<sub>6</sub>, m. 181–5°. Silver salt, white flocculent ppt. becoming black in the air. *p*-Dimethylamino- $\beta,\beta$ -phenyl-*o*-tolylisossuccinic acid, almost insol. in C<sub>6</sub>H<sub>6</sub> and petr. ether, slightly sol. in Et<sub>2</sub>O and cold EtOH, brilliant white crystals, m. 183° with loss of CO<sub>2</sub>; silver salt, white gelatinous ppt., becoming brown in the light. On heating the above acid alone, or heating the reaction mixt. from which it is formed with AcOH, *p*-dimethylamino- $\beta,\beta$ -phenyl-*o*-tolylpropionic acid is formed, slightly sol. in Et<sub>2</sub>O and petroleum ether, sol. in warm EtOH and C<sub>6</sub>H<sub>6</sub>, large colorless crystals from EtOH, m. 158–60°. Silver salt, flocculent white ppt. becoming gray in the light. *p*-Dimethylamino- $\beta,\beta$ -phenyl-*p*-tolylisossuccinic acid, difficultly sol. in C<sub>6</sub>H<sub>6</sub> and petr. ether, slightly sol. in cold EtOH and in Et<sub>2</sub>O, small white needles from hot EtOH, m. 193° with loss of CO<sub>2</sub>; silver salt, white ppt., soon becoming brown in the light. On heating to 160–198°, the acid loses CO<sub>2</sub> and forms *p*-dimethylamino- $\beta,\beta$ -phenyl-*p*-tolylpropionic acid, slightly sol. in Et<sub>2</sub>O, easily sol. in EtOH and warm C<sub>6</sub>H<sub>6</sub>, brilliant white crystals, m. 173–5°; silver salt, white flocculent ppt., becoming brown in the air. *p*-Dimethylamino- $\beta,\beta$ -phenyl- $\alpha$ -naphthylisossuccinic acid, almost insol. in C<sub>6</sub>H<sub>6</sub> and



petr. ether, slightly sol. in cold EtOH and Et<sub>2</sub>O, small white needles from boiling EtOH, m. 172° with loss of CO<sub>2</sub> and solidifying, m. again 185°, which is the m. p. of *p*-dimethylamino- $\beta$ , $\beta$ -phenyl- $\alpha$ -naphthylpropionic acid (Fosse, *loc. cit.*), sol. in warm EtOH and C<sub>6</sub>H<sub>6</sub>, slightly sol. in Et<sub>2</sub>O and petr. ether, white crystals, with a pink tint, m. 183-5°, *silver salt*, white ppt. rapidly turning brown. *p*-Dimethylamino- $\beta$ , $\beta$ -phenyl-*p*-nitrophenylpropionic acid, insol. in petroleum ether, slightly sol. in Et<sub>2</sub>O, easily sol. in warm C<sub>6</sub>H<sub>6</sub> and EtOH, golden yellow prisms, m. 179-80°; *silver salt*, yellow flocculent ppt., becoming greenish brown in the light; *methyl ester*, orange-yellow prisms, m. 91-2°; *chloroplatinate of methyl ester*; *ethyl ester*; *chloroplatinate of ethyl ester*. *p*-methylamino- $\beta$ , $\beta$ -phenyl-*m*-nitrophenylpropionic acid, golden yellow prisms from EtOH, m. 143-5°; *silver salt*, light yellow flocculent ppt., becoming greenish brown in the light; *methyl ester*; *chloroplatinate of methyl ester*; *ethyl ester*, yellow prisms, m. 67-8°; *chloroplatinate of ethyl ester*. M. R. SCHMIDT

**Separation of the  $\beta$ -naphthylaminemonosulfonic acids.** GIORGIO RENATO LEVI. *Giorn. chim. ind. applicata* 3, 97-101 (1921).—In his expts. L. prepd.  $\beta$ -C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> by heating 5 parts  $\beta$ -naphthol, 2 parts (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and 10 parts 20% Ag aq. NH<sub>4</sub>OH in an autoclave, bringing to 150° during 4 hrs. and maintaining at this temp. for 6 hrs. with const. agitation. The sulfonation was carried out directly upon the product without previous distn. The sulfonation product contained 35% of the 2,8-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)SO<sub>3</sub>H and 65% of the 2,5- (mixed with the 2,6- and the 2,7-) acids. L. devised a method of sepg. the 2,8- from the 2,5- mixed with 2,6- and 2,7- acids. His method consisted in dissolving the mixed acids in *N* NaOH and pptg. the soln. fractionally with *N* H<sub>2</sub>SO<sub>4</sub>. The acid was introduced slowly, about 1/2 hr., and the ppt. still agitated for about an hr., while in the liquid, then filtered, washed on the filter by the pump, the washing liquid added to the principal liquid after previous concn. From his expts. L. concluded that the product sepd. from a mixt. of the Na salts of the isomers by adding slowly the theoretical amt. of H<sub>2</sub>SO<sub>4</sub> to ppt. all the 2,8- acid present, is practically pure 2,8- acid. ROBERT S. POSMONTIER

**Reaction of naphthols and naphthylamines with bisulfite.** P. FRIEDLÄNDER. Kaiser-Wilhelm-Inst. f. physik. Chem. u. Elektrochem. *Ber.* 54B, 620-4 (1921).—According to Bucherer in the reaction which bears his name, but which should more properly be called the Lepetit-Bucherer reaction, NaHSO<sub>3</sub> reacting on C<sub>10</sub>H<sub>7</sub>OH (or on C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> with evolution of NH<sub>3</sub>) first forms C<sub>10</sub>H<sub>7</sub>OSO<sub>3</sub>H, which is quite stable towards dil. mineral acids but is hydrolyzed with extraordinary ease by alkalis and with NH<sub>3</sub> and amines gives naphthylamines; analogous sulfurous esters are assumed to be formed as intermediate products in the reaction with substituted naphthols and naphthylamines. The exptl. basis for this view, however, is meager and has but little force. B. did not succeed in isolating the intermediate products, which are generally very sol., in sufficiently pure state and in analyzing them with decisive results. Their striking reactivity does not agree at all with the behavior of the neutral phenol and naphthol esters of H<sub>2</sub>SO<sub>4</sub>, which have since been prepd. from phenols and SOCl<sub>2</sub>. Still more doubtful is B.'s explanation of the process whereby naphthocarbazoles are formed from naphthols, NaHSO<sub>3</sub> and PhNHNH<sub>2</sub>; e. g., in the case of  $\beta$ -C<sub>10</sub>H<sub>7</sub>OH he assumes the following intermediate stages: C<sub>10</sub>H<sub>7</sub>OSO<sub>3</sub>H  $\rightarrow$  C<sub>10</sub>H<sub>7</sub>NNHPh  $\rightarrow$  C<sub>10</sub>H<sub>7</sub>N-NPh  $\rightarrow$  C<sub>10</sub>H<sub>7</sub>N(SO<sub>3</sub>H)NHPh  $\rightarrow$  C<sub>10</sub>H<sub>6</sub>N(SO<sub>3</sub>H)C<sub>6</sub>H<sub>5</sub>  $\rightarrow$  C<sub>12</sub>H<sub>9</sub>NH C<sub>6</sub>H<sub>5</sub>.

Against this explanation, besides the improbability of the formation of an azo from a hydrazo compd. in the presence of NaHSO<sub>3</sub>, is the fact that the supposed *N*-sulfonic acid of carbazole smoothly splits off H<sub>2</sub>SO<sub>4</sub> and not H<sub>2</sub>SO<sub>3</sub> on decompn. with acids or alkalis. All these difficulties disappear if it is assumed (cf. Vorozhtzov, *C. A.* 10, 2896; Lebedev, *Diss. Dresden* 1914) that the naphthols and their substitution products



do not react with  $\text{NaHSO}_4$  in their stable enol but in their keto forms; even if these are present in only very small amt. they react almost completely on long boiling with  $\text{NaHSO}_4$  because they are attacked by the  $\text{NaHSO}_3$  and the equil. with the enol form is reestablished. The resulting compds. with the grouping  $-\text{CH}_2\text{C}(\text{OH})\text{OSO}_2\text{Na}$  show the well known reactivity of the ketone-bisulfite addition products towards primary amines and hydrazines and easily explain all the transformations in the Lepetit-Bucherer reaction. They differ from B.'s assumed intermediate products by 1 mol. of  $\text{H}_2\text{O}$ , a difference which cannot be detd. definitely by analysis of very easily sol., in part hygroscopic and not completely salt-free compds. The product from  $\beta$ -naphthol,  $\text{NaHSO}_3$  and  $\text{PhNHNH}_2$  can be purified somewhat more easily; according to B. it has the compn.  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{NSNa}$  while according to the view adopted by F. it should have the compn.  $\text{C}_{10}\text{H}_{12}\text{C}_6\text{NSNa}$ ; the calcd. H content for the 2 formulas is 3.48 and 4.15, resp.; found, 4.2%. But which of the two formulas is correct can be detd. in another way; according to the first the formation of an analogous compd. from *N*-alkyl-*N*-phenylhydrazines is not possible. As a matter of fact, when 19 g. 2,3- $\text{C}_{10}\text{H}_6(\text{OH})\text{CO}_2\text{H}$  in  $\text{NaOH}$  is treated with 13 g.  $\text{MeNPhNH}_2$  and 120 cc. of 36%  $\text{NaHSO}_3$ , the reaction proceeds exactly as with  $\text{PhNHNH}_2$  (B. and Seyde, *J. prakt. Chem.* [2] 77, 403) and there is formed *N*-methyl-naphthophenocarbazole (A), needles, m.  $121^\circ$ , dissolves in the usual solvents with blue fluorescence; *picrate*, red needles, m.  $171^\circ$ . The constitution of A is established by the fact that it is not attacked by  $\text{KOH}$  at  $230^\circ$  while under the same conditions naphthocarbazole gives a K salt which with  $\text{MeI}$  yields A. CHAS. A. ROUILLER

**Tolunaphthol** [ $\beta$ -naphthyl *p*-toluate]. G. J. ÖSTLING. *Zig. finn. Apoth.* 1918.— *$\beta$ -Naphthyl *p*-toluate*, prepd. from *p*-toluic acid and  $\beta$ -naphthol, is a white powder, m.  $137^\circ$  (from alc.). Unlike  $\beta$ - $\text{C}_{10}\text{H}_7\text{OBz}$ , it is not resolved into its components by the action of pancreas infusion. J. C. S.

**The acetone-naphthols.** K. FRIES. *Techn. Hochschule Braunschweig. Ber.* 54B, 709-14 (1921).—Witt and Braun obtained, through its Me ether, by condensation of nerolin with  $\text{AcCl}$ , an *o*-aceto- $\beta$ -naphthol (A), m.  $640^\circ$ , to which they assigned the structure 2,3- $\text{C}_{10}\text{H}_6(\text{OH})\text{Ac}$  because "it smoothly and easily forms azo dyes with diazonium compds.," a reaction which they believed to be given by  $\beta$ -naphthol derivs. only when the  $\alpha$ -position is free (C. A. 9, 803). 1,2- $\text{C}_{10}\text{H}_6(\text{OH})\text{Ac}$  (B) is best obtained (80% yield) by W. and B.'s method; the rearrangement of  $\alpha$ - $\text{C}_{10}\text{H}_7\text{OAc}$  by heating with  $\text{AlCl}_3$  yields at best (from equal parts acetate and  $\text{AlCl}_3$  heated 4 hrs. at  $125^\circ$ ) 50% B., together with some 1,2,4- $\text{C}_{10}\text{H}_5(\text{OH})\text{Ac}$ , m.  $141^\circ$ . The acetate of B m.  $107^\circ$ . *Methyl ether*, best prepd. with  $\text{Me}_2\text{SO}$  and 2 *N*  $\text{NaOH}$  allowed to stand 24 hrs. at room temp., table-like crystals from dil. alc., m.  $49^\circ$ , sol. in concd.  $\text{H}_2\text{SO}_4$  with yellow color. When 50 g.  $\beta$ - $\text{C}_{10}\text{H}_7\text{OAc}$  in 100 cc.  $\text{CS}_2$  is slowly treated in ice with 50 g.  $\text{AlCl}_3$  heated 1 hr. under a reflux on the  $\text{H}_2\text{O}$  bath, freed from the  $\text{CS}_2$  by distn., again heated 4 hrs. at  $120^\circ$ , decompd. with  $\text{H}_2\text{O}$ , dissolved in  $\text{NaOH}$  on the  $\text{H}_2\text{O}$  bath, treated with charcoal and acidified, there is obtained 40% of *1-aceto-2-naphthol* (C), light yellow needles or rhombic tables from gasoline, m.  $64^\circ$  (mixed with A, it begins to m.  $40^\circ$ ), forms easily sol., intensely yellow alkali salts, dissolves in concd.  $\text{H}_2\text{SO}_4$  with yellow color; *methyl ether*, prepd. with  $\text{Me}_2\text{SO}$  in 2 *N*  $\text{NaOH}$  at room temp., faintly yellow prisms from  $\text{Et}_2\text{O}$ , m.  $59^\circ$ , sol. in concd.  $\text{H}_2\text{SO}_4$  with yellow color; *carboxy derivative* (D), similarly prepd. with  $\text{ClCO}_2\text{Et}$ , stout needles from alc., m.  $60^\circ$ , pptd. unchanged by  $\text{H}_2\text{O}$  from its yellow soln. in  $\text{H}_2\text{SO}_4$ , quite stable towards soda and dil.  $\text{NaOH}$ . C (1.86 g.) in  $\text{CHCl}_3$  treated with 1.6 g. Br, freed from the  $\text{CHCl}_3$  by evapn., stirred with alc., filtered, treated with dil. soda, again filtered and pptd. with  $\text{HCl}$  gives, not the expected  $\text{C}_{10}\text{H}_6(\text{OH})\text{COCH}_2\text{Br}$ , but 2,1- $\text{C}_{10}\text{H}_6(\text{OH})\text{Br}$ , m.  $82^\circ$ . Likewise, when 3 g. C in 1.3 g.  $\text{NaOH} + 1$  g. soda in 150 cc.  $\text{H}_2\text{O}$  is treated at room temp. with the diazotized soln. of 3.4 g. sulfanilic acid, the Ac group is displaced and there is formed  $\beta$ -naphthol orange. This

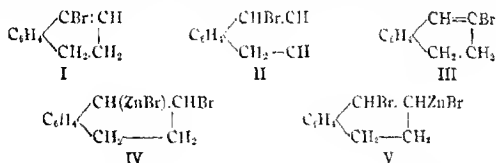


property of coupling with diazonium compds. is shared with other  $\beta$ -naphthol derivs. substituted in the 1-position, so the evidence advanced by W. and B. in favor of the structure they assigned to A is without force. Since, however, A is not identical with C, their formula for A, although deduced by them without any valid evidence, is correct. *1-o-Bromoaceto-2-naphthyl ethyl carbonate*, from 2.6 g. D in 12 cc.  $\text{CHCl}_3$  and 1.6 g. Br in 5 cc.  $\text{CHCl}_3$ , fine tables from benzene, m.  $79^\circ$ , very soon deposits AgBr when boiled in aq. alc. with  $\text{AgNO}_3$ . *Glycolic acid 2-[1-acetonaphthyl] ether*, from 18.6 g. C and 8 g. NaOH in 120 cc.  $\text{H}_2\text{O}$  boiled 2 hrs. under a reflux with 9.5 g.  $\text{ClCH}_2\text{CO}_2\text{H}$ , leaflets from  $\text{C}_6\text{H}_6$ , m.  $145^\circ$ , easily sol. in dil. soda and  $\text{NH}_4\text{OH}$ ; 4 g. heated at  $180-90^\circ$  until the evolution of  $\text{CO}_2$  ceases and then a short time at  $210^\circ$  and treated with soda yields 0.35 g.  $\beta\text{-C}_{10}\text{H}_7\text{OCH}_2\text{CO}_2\text{H}$ , m.  $155^\circ$ , sol. in the soda, and 1.8 g. 3-methyl-4,5-benzocoumarone, m.  $59^\circ$ , which does not dissolve in the soda. This synthesis of the coumarone (cf. Stoermer, *Ann.* 312, 311(1900)) affords a proof, which up to the present was lacking, of the correctness of the structure assigned to it. C. A. R.

**Benzopolymethylene compounds. II. Brominated alicyclic substitution products of tetrahydronaphthalene (tetralin) and  $\Delta^1$ -dihydronaphthalene ( $\Delta^1$ -dialin).** JULIUS V. BRAUN AND GEORG KIRSCHBAUM. Landw. Hochschule Berlin. *Ber.* 54B, 597-618 (1921); cf. C. A. 14, 3659.—Unlike hydrindene, tetrahydronaphthalene (A) behaves towards Br as a perfect analog of an alkylated  $\text{C}_{10}\text{H}_8$ ; in the cold and the dark there is hardly any reaction; in the presence of a little Fe or, better, a trace of I, the  $\text{C}_6\text{H}_4$  nucleus is easily substituted, even at  $-10^\circ$ , with the formation of a mixt. of  $\alpha$ - and  $\beta$ -bromotetrahydronaphthalenes; at higher temps. without a catalyzer or when illuminated, the Br attacks the hydrogenated ring. A peculiarity of the alicyclic bromination of A as compared with PhMe and its homologs is, first, that it occurs more easily, being as rapid at  $100^\circ$  as that of the xylenes at  $120-30^\circ$ , and, second, that, contrary to the dialkybenzenes, monosubstitution cannot be effected; there is always formed a dibromide which proved to be the  $\alpha,\beta$ -compd., A therefore behaving, not like *o*-xylene but like PhEt. A in boiling  $\text{H}_2\text{O}$  is treated with 4 atoms Br as rapidly as the latter disappears (about 30 min. for 150 g. A and 365 g. Br), shaken with ice  $\text{H}_2\text{O}$ , taken up in a little  $\text{Et}_2\text{O}$ , dried with  $\text{CaCl}_2$ , freed from most of the  $\text{Et}_2\text{O}$  and placed in the ice chest; in 12 hrs. the cryst. mass is drained off and washed with a little ice-cold alc., giving almost 50% of  $\alpha,\alpha,\beta,\beta$ -dibromotetralin (B), crystals from  $\text{CHCl}_3\text{-EtOH}$ , m.  $70^\circ$ , b.p.  $165-73^\circ$ .  $\text{EtOH}$  in MeOH (Straus and Lemmel, C. A. 7, 1499) converts B into a mixt. of a little C;  $\text{H}_2$  and touch of an oil with a ketone odor, and alc. NaOEt produces a similar change except that in this case the  $\text{C}_{10}\text{H}_8$  predominates by far. Tertiary amines (NMe<sub>3</sub>, PhNMe<sub>3</sub>,  $\text{C}_6\text{H}_5\text{N}$ ) have hardly any action on the  $\text{H}_2\text{O}$  bath; primary and sec. aromatic amines (PhNH<sub>2</sub>, PhNHMe) give viscous Br-free products, hardly sol. in dil., somewhat sol. in concd. acids, which from their whole behavior seem to be products of high mol. wt. formed by combination of several B mols. through nitrogenous residues. Finally, with sec. bases like  $\text{NH}_2\text{Et}$  or piperidine it is possible to remove a mol. of HBr quite smoothly. Thus, 1 mol. B is slowly added to 3 mols. ice-cold piperidine, allowed to stand overnight in running  $\text{H}_2\text{O}$ , heated 2 hrs. on the  $\text{H}_2\text{O}$  bath, treated with dil. acid, taken up in  $\text{Et}_2\text{O}$ , dried with  $\text{CaCl}_2$  and fractionated *in vacuo*, giving about 80% of a bromodialin (I, II or III) (as the term "tetralin" for 1,2,3,4-tetrahydronaphthalene is now generally used in the technical literature, v. B and K. propose the name "dialin" for dihydronaphthalene), which after repeated careful fractionation forms an odorless, almost colorless liquid gradually becoming yellowish, does not solidify even on strong cooling, b.p.  $130-40^\circ$ ; analysis indicates that it is still contaminated with a little  $\text{C}_{10}\text{H}_8$  (found, C 58.38, H 4.71, Br 37.42%; calcd., 57.41, 4.31, 38.28%, resp.), but with Br in  $\text{CS}_2$  it gives almost quant. an analytically pure bromine addition product,  $\text{C}_{10}\text{H}_8\text{Br}_2$ , leaflets from  $\text{CHCl}_3\text{-EtOH}$ .



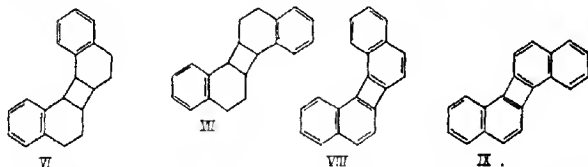
m. 71°. The product is so homogeneous that v. B. and K. are inclined to believe that the liquid bromodialin is also a chem. individual, *i. e.*, that B, unlike dibromostyrene, splits off HBr in only one way; whether it is the  $\alpha$ - or the  $\beta$ -Br atom which is eliminated is at present uncertain; on treating the bromodialin in MeOH with PdCl<sub>2</sub>, gum arabic and H<sub>2</sub>, the smooth absorption of H proceeds with undiminished rapidity after 2 atoms of H have been taken up; if the reaction is interrupted at this point, the product is found to consist of a mixt. of A and unchanged bromodialin. Like Straus (*C. A.* 7, 2554), v. B. and K. find that B, unlike the  $\beta, \beta'$ -dibromotetralin, does not quant. lose Br to form  $\Delta^1$ -dialin with Zn filings in alc., even when the temp. and the velocity of addition of the B to the Zn-EtOH mixt. are varied. If the reaction is allowed to proceed a long time (2.5 hrs.) at 60° the product is free of Br, to be sure, but titration with Br shows that it contains but 80% of the dialin; the other 20% is a less volatile by-product apparently consisting of a mixt. of several hydrocarbons whose compn. corresponds very closely to that of dialin. The action of the Zn is much more energetic in HO-free solvents (C<sub>6</sub>H<sub>6</sub>, Et<sub>2</sub>O, Me<sub>2</sub>CO); when Zn filings are added to such a soln. there is a vigorous reaction, the Zn dissolves, and the soln. becomes turbid and brownish, then yellow; gradually an intense yellow-green fluorescence appears and when almost all of the Zn has been added and the mixt. is heated on the H<sub>2</sub>O bath the turbidity disappears; H<sub>2</sub>O is now added (Et<sub>2</sub>O, when Me<sub>2</sub>CO is used) and the Et<sub>2</sub>O layer dried with CaCl<sub>2</sub>; this soon produces a turbidity and deposition on the CaCl<sub>2</sub> of a deep yellow powder (see C below) which can easily be removed mechanically. Evapn. of the Et<sub>2</sub>O gives a rather thick oil yielding *in vacuo* some  $\Delta^1$ -dialin up to 100%; the temp. then rises slowly and at 240–65° there dists. over an exceedingly viscous, faintly yellow oil gradually solidifying to a glass on cooling and having very nearly the compn. of dialin but doubtless not homogeneous. The residue in the distn. flask solidifies to a viscous honey-yellow mass pptd. from CHCl<sub>3</sub> by EtOH as a fine deep yellow powder identical with the product C (see above). After 2 further pptns. from CHCl<sub>3</sub>, digestion for a short time in hot C<sub>6</sub>H<sub>6</sub> with charcoal and cautious pptn. with alc. it forms a bright yellow powder, sinters 212°, m. 220°, with the same compn. as dialin but a mol. wt. about 8 times as large (955–73 in freezing C<sub>6</sub>H<sub>6</sub>). Special expts. showed that the pure dialin undergoes some change, to be sure, but only to a very small extent, when boiled a long time in Et<sub>2</sub>O with ZnBr<sub>2</sub> or ZnCl<sub>2</sub>; v. B. and K. therefore believe that in the above polymerization there are formed at the first instant metallo-organic complexes (IV or V) which change extramolecularly, with loss of ZnBr<sub>2</sub>. As compared



with styrene,  $\Delta^1$ -dialin is stable towards light and heat. Weeks' exposure to daylight and repeated distn. do not change it, but it can be polymerized by energetic chem. agents. Thus, when dild. with 10 parts of an ice-cold satd. hydrocarbon (C<sub>6</sub>H<sub>6</sub>, petr. ether), vigorously stirred, slowly treated with an equal wt. of concd. H<sub>2</sub>SO<sub>4</sub>, allowed to stand 2 hrs. at room temp., dild. with H<sub>2</sub>O, freed from the solvent used as diluent with steam, taken up in Et<sub>2</sub>O, dried and distd. *in vacuo*, there is obtained almost quant. *bisdialin* (VI or VII), b<sub>12</sub> 243–5°, mol. wt. in freezing C<sub>6</sub>H<sub>6</sub> 243, forms after very long standing in the ice chest crystals, which after repeated crystn. from alc. m. 93°. When either the solid or the oily substance is distd. in CO<sub>2</sub> over PbO there is obtained



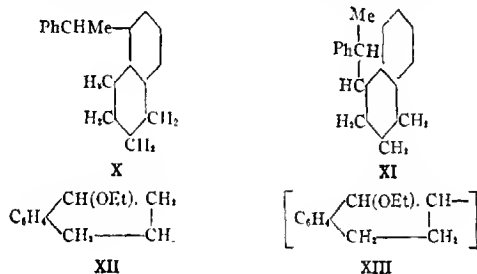
a distillate which partially solidifies and from which small amts. of  $C_{16}H_{10}$  and A can be sepd. with steam. The non-volatile, semisolid part is converted by washing with a little cold alc. into a solid yellow powder identical in both cases but formed in far greater proportion from the crystd. (60-70%) than from the oily (10-20%) bisdialin; after several crystns. from alc. it forms a fine yellow powder,  $C_{20}H_{14}$ , m.  $165^{\circ}$ , mol. wt. in freezing  $C_6H_6$ , 264, and is undoubtedly *bisnaphthylene* (VIII or IX). From the fact that it is formed in such larger amt. from the crystd. bisdialin, it is concluded that what prevents the crystn. of the liquid bisdialin are not small amts. of impurities, hardly detectable by analysis, but an isomer, much more difficult to cryst., of the  $93^{\circ}$  form. Attempts to confirm the structures VI or VII by oxidative degradation showed, as was expected, that energetic oxidation ( $KMnO_4$ ) gave phthalic acid; as an intermediate product, phthalonic acid, m.  $143^{\circ}$ , was identified in 2 cases. Whether any bisdialin is formed in the action of Zn on B cannot be stated with certainty; possibly it is present in the  $240-665^{\circ}$  fraction of the product. The bisnaphthylidene is also



obtained when bistetralin is heated with 2 atoms of S at  $205^{\circ}$  until the evolution of  $H_2S$  ceases. Following Kramer and Spilker's method (*Ber.* 24, 2785(1891)), it was found that styrene and A form a condensation product (X or XI), quite viscous, only faintly colored oil,  $b_p$   $221.5^{\circ}$ , does not solidify even after weeks of cooling; from its b. p. it is concluded that no similar products are present in the mixts. of dialin and the diluent hydrocarbon used in the above prepn. of bisdialin and that the autocondensation of the dialin is almost entirely the sole reaction.  $\Delta^1$ -Dialin may easily and almost quant. be obtained from B by the Grignard reaction; moisture does not interfere; so ordinary may be used instead of abs.  $Et_2O$ , although the alc. must be washed out and if the B has been purified from  $CHCl_3$ - $EtOH$  it must be thoroughly dried completely to remove any alc. The B in about 5 parts  $Et_2O$  is treated with a small portion of 1 atom of Mg, then with a trace of I to start the reaction; the rest of the Mg is added as it is used up and the mixt. finally heated a short time on the  $H_2O$  bath and then decompd. with ice  $H_2O$  and dil. acid. The dialin  $b_p$   $91^{\circ}$ , regenerates B quant. with Br in  $CS_2$ , m.  $-8^{\circ}$ ,  $d_4^{25}$  0.9963, has a much more intense odor than A. B under 3 parts  $H_2O$  on the  $H_2O$  bath treated with  $Me_2CO$  (about 4.5 parts) until a clear soln. results, then boiled 7 hrs., freed from most of the  $Me_2CO$  and dild. with much  $H_2O$  gives almost quant. *ac-a-hydroxy- $\beta$ -bromotetralin*, crystals from dil. alc., m.  $112^{\circ}$ , regenerates B when satd. in  $C_6H_6$  with  $HBr$ , allowed to stand 1 day, concd. with gentle heat and rubbed with cold alc.; with alc.  $KOH$  it loses  $HBr$  and forms the dialin oxide. *ac-Alkoxy- $\beta$ -bromotetralins* are easily obtained by heating B with 4-5 parts of the appropriate alc. on the  $H_2O$  bath (1-5 hrs. with the lower ales., longer with the higher ales.), pptg. with  $H_2O$  and taking up in  $Et_2O$ ; the following were so prepd.: *Methoxy*,  $b_p$   $151.2^{\circ}$ , has a faint ester odor; *ethoxy*,  $b_p$   $171-2^{\circ}$ ; *amyloxy* (obtained pure only after 15 hrs. heating),  $b_p$   $175-80^{\circ}$ , has a faint Am odor and is faintly yellow; *allyloxy*,  $b_p$   $171^{\circ}$ , smells very faintly of allyl alc., easily absorbs 1 mol. Br in indifferent solvents ( $CHCl_3$ ,  $CS_2$ ) but forms an oily product. These ethers become faintly brown on standing, the accompanying decompn. is too slight to be detected by analysis or distn. but is shown by the behavior in the Grignard reaction; the freshly distd. products react



with Mg in dry Et<sub>2</sub>O with about the same ease as EtBr but after 2 days their reactivity is markedly diminished, although they are still colorless, and if they are allowed to stand until the faint brown color is perceptible they no longer react at all with the Mg. The course of the reaction was studied with the Et ether. If it is treated with 1 atom Mg, first in the cold and then 0.5 hr. on the H<sub>2</sub>O bath, usually part of the Mg remains undissolved and on decompn. with dil. acid there is obtained a liquid, halogen-free product sepd. by distn. chiefly into 2 parts: a fraction b<sub>14</sub> 97–145° (chiefly 97–100°) having the compn. of dialin mixed with a substance still containing O (found, C 90.21, H 8.1%), and a fraction b<sub>15</sub> 255–60° with the compn. of bisdialin mixed with an O compd. (found, C 87.90, H 7.8%). It is evident that there are formed the ethers XII and XIII which partially go over into dialin and hisdialin. Attempts to isolate these ethers in pure form failed; on distn. there is a partial elimination of alc. which can be made complete by boiling with dil. H<sub>2</sub>SO<sub>4</sub>. If the second of the above fractions is allowed to stand a long time in the cold pure  $\beta,\beta'$ -bisdialin seps. out and crysts. from alc. in leaflets, m. 156°; its alc. soln. has a violet fluorescence; it is most easily prepd. by decomp. the product of the reaction of Mg on the Br ether with dil. acid, heating on the H<sub>2</sub>O bath with H<sub>2</sub>SO<sub>4</sub> and alc., removing the dialin with steam and crystg. the solid residue from alc. With Na and alc. it is easily reduced to  $\beta,\beta'$ -bis-



tetralin, leaflets from alc., m. 113°; distd. over PbO it gives  $\beta,\beta'$ -dinaphthyl, m. 186°, which is also obtained quant. when the bisdialin in CHCl<sub>3</sub> is treated with 2 mols. Br; the Br is immediately absorbed and at once split off again as HBr. All attempts to obtain XIII by reduction of the ethoxybromotetralin have thus far failed; Zn and alc. were without action; catalytic reduction gave A; Zn and HCl yielded dialin or its polymers. B gently boiled 3–4 min. with 1 part KOAc in 4 parts AcOH, quickly cooled and treated with cold H<sub>2</sub>O gave almost quant.  $\alpha$ -acetoxy- $\beta$ -bromotetralin, needles from alc., m. 95–6°, converted by short digestion with fuming HCl and alc. into AcOEt and  $\alpha$ -hydroxy- $\beta$ -bromotetralin. When Cl is passed into A at 100° until 2 atoms have been absorbed there is obtained an oil which does not solidify on cooling for days and on fractionation yields a chief fraction (about 70% of the calcd. amt.) b<sub>23</sub> 155–60°, having very nearly the compn. of dichlorotetralin (found, 34.2% Cl) and giving, when dropped into Zn filings and alc. at 60°, up to 50% of  $\Delta^1$ -dialin. CHAS. A. ROULLIER

**Anthracene series.** I. EDWARD DEBARRY BARNETT AND JAMES WILFRED COOK. Sir John Cass Tech. Inst. *J. Chem. Soc.* 119, 901–13 (1921).—Several cases are known in which the formation of a pyridinium salt is accompanied by a weakening of the C<sub>4</sub>H<sub>5</sub>N ring, so that when the salt is treated with a base, the ring is opened and a deriv. of glutaric aldehyde formed. The present study is concerned with pyridinium salts containing the C<sub>14</sub>H<sub>10</sub> ring. *9,10-Dihydroanthraquinylidipyridinium dibromide* (A), C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>Br<sub>2</sub>·6H<sub>2</sub>O, from C<sub>4</sub>H<sub>5</sub>N and C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>, or more conveniently by suspending



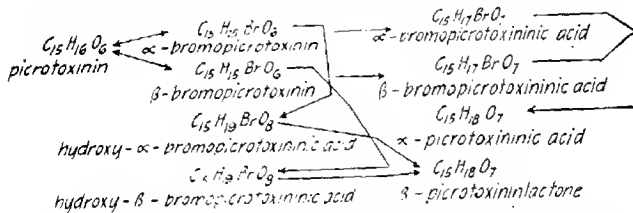
180 g. tech.  $C_{14}H_{10}$  in 1800 cc.  $C_6H_5N$ , slowly adding 480 g. Br at about  $4^\circ$ , and reducing the perbromide by boiling with  $Me_2CO$ , cryst. powder from  $H_2O$ , with 6  $H_2O$ , or large transparent needles with 5  $H_2O$  when the aq. soln. in concd. in a desiccator; anhydrous, from alc.- $Et_2O$ , m.  $166-7^\circ$ . *Perbromide*,  $C_{24}H_{20}N_2Br_8$ , orange-red powder. *Periodide*, violet powder. *Hydrogen chromate*,  $C_{24}H_{20}N_2 \cdot 2HCrO_4$ , orange needles. *Picrate*,  $C_{24}H_{20}O_{14}N_8$ , m.  $168.5-170^\circ$ . Heated on the  $H_2O$  bath in a stream of  $CO_2$  for 4 hrs., a nearly quant. yield of anthrone was obtained (a convenient method for the prepn. of this compd.). When 35 g. A in 500 cc.  $H_2O$  at  $15^\circ$  are treated with 100 cc.  $0.5 N NaOH$ , *anthranilpyridinium bromide*,  $C_{13}H_{11}NBr \cdot H_2O$ , (B) is formed, lemon-yellow leaflets or needles with 1  $H_2O$ , which loses its  $H_2O$  rapidly at  $150^\circ$ . *Perbromide*,  $C_{13}H_{10}ONBr_3$ , orange-red needles from MeOH. *Dichromate*,  $(C_{13}H_{11}N)_2Cr_2O_7$ , orange-red needles. *Picrate*, yellow needles, m.  $180-2^\circ$ . B was also obtained by the action of  $NH_3$ ,  $MeNH_2$ ,  $Me_2NH$ ,  $C_2H_5N$ ,  $C_3H_7N$ , and piperidine upon A. *g-Phenylamino-g,10-dihydroanthracene*,  $C_{20}H_{17}N$ , by boiling A with or without alc. with  $PhNH_2$ , yellow leaflets, m.  $197-200^\circ$ . *g-o-Nitrophenylamino derivative*,  $C_{20}H_{15}O_3N_2$ , from A and *o-O\_2NC\_6H\_4NH\_2*, glistening brick-red needles, m.  $219-20^\circ$ . *g-m-Nitrophenylamino derivative*, bright red needles, m.  $199-200^\circ$ . *g-p-Nitrophenylamino derivative*, lemon-yellow needles, m.  $179-80^\circ$ . *g-o-Tolylamino derivative*,  $C_{21}H_{15}N$ , lemon-yellow needles, m.  $158-60^\circ$ . *g-p-Tolylamino derivative*, minute yellow needles, m.  $160-2^\circ$ . *g-o-Carboxyphenylamino derivative*,  $C_{21}H_{13}O_3N$ , glistening yellow crystals, decomp.  $255-75^\circ$ . *g-p-Benzeneazo-phenylamino derivative*,  $C_{24}H_{15}N_3$ , yellowish brown needles, m.  $230.5-31.5^\circ$ . *g- $\beta$ -Naphthylamino derivative*, m.  $182-207^\circ$ . *g-Phenylmethylamino derivative*,  $C_{24}H_{19}N$ , yellow needles, m.  $141.5-43.5^\circ$ . *g-Phenylamino derivative*, from  $Ph_2NH$  and A,  $C_{25}H_{21}N$ , greenish yellow leaflets, m.  $226-7.5^\circ$ .

C. J. WEST

**Picrotoxin. X. Degradation of  $\alpha$ -picrotinic acid,  $C_{15}H_{17}O_7$ , to the acid  $C_{13}H_{14}O_4$ .** P. HORRMANN AND M. HAGENDORN. *Arch. Pharm.* 259, 7-15 (1921); cf. C. A. 15, 1899. — $\alpha$ -Picrotinic acid, obtained by protracted boiling of picrotin with dil. aq. mineral acids, is the result of purely hydrolytic change, i. e., picrotin,  $C_{15}H_{17}O_7$ , +  $H_2O$  =  $\alpha$ -picrotinic acid,  $C_{15}H_{17}O_8$ . Alc. alkali effects a similar change, in that an ester of the acid results, as also one of  $\beta$ -picrotinic acid. On boiling  $\alpha$ -picrotinic acid with  $40-45^\circ$   $H_2SO_4$ , a resinous mass was obtained which consisted of at least 2 products, picrotinketol,  $C_{15}H_{16}O_4$  (previously reported by Angelico, C. A. 5, 1092), and a substance difficultly sol. in  $Et_2O$  as yet unidentified. The ketol (*oxime*,  $C_{15}H_{16}O_2 \cdot NOH$ , m.  $206^\circ$  (decompn.), *semicarbazone*,  $C_{15}H_{16}O_2 \cdot NNHC(=NH)_2$ , decomp.  $226^\circ$ , *acetate*,  $C_{15}H_{15}O_4 \cdot COCH_3$ , m.  $84^\circ$ , *osazone* m.  $204^\circ$ ) yields on oxidation with  $KMnO_4$  not an acid  $C_{14}H_{14}O_4$ , as stated by Angelico, but one having the compn.  $C_{13}H_{14}O_4$ , likewise 2 neutral compds., of which one is volatile with steam, crystals, m.  $84^\circ$ . The acid  $C_{13}H_{14}O_4$  (silver salt  $C_{13}H_{12}O_4 \cdot Ag$ ), fine needles m.  $165^\circ$ . The degradation of the ketol  $C_{15}H_{16}O_4$  to the acid  $C_{13}H_{14}O_4$  permits some conclusion relative to the constitution of the oxidized portion of the ketol mol. Of the 3 possible formulas: (I)  $C_{13}H_{14}O_4 \cdot CH(OH)CHO$ , (II)  $C_{13}H_{14}O_4 \cdot COCH_2OH$  and (III)  $(C_{13}H_{14}O_4 \cdot R)COCH(OH)$ , the 3rd is excluded for the reason that the resulting acid could not have 13 C atoms; of the remaining formulas, the authors favor the 2nd or ketone form in spite of the fact that the ketol possesses the power to reduce  $NH_4 \cdot AgNO_3$ . **XI. Behavior of bromopicrotoxin toward concentrated hydrogen halides.** P. HORRMANN AND W. BERTSCHMIDT. *Ibid* 69-93. —On account of the questionable composition of the bromopicrotoxin employed by Siefisch in his work (cf. C. A. 7, 345) on the behavior of this substance toward  $HCl$  and  $HBr$ , H. and B. undertook the investigation anew along similar lines, notably the effect of the concd. acids ( $HCl$  and  $HBr$ ), as also  $HNO_3$ , on both  $\alpha$ -bromopicrotoxin (A) and  $\beta$ -bromopicrotoxin (B), since it did not appear improbable that the Br compds. obtained by S. might prove on dehalogenation to be derivs. of picrotin. The action, e. g., of concd.



HCl on **B** at the boiling temp. leads to the formation of hydroxy- $\beta$ -bromopicrotoxininic acid. The yield obtained by **S**. (42%) can be increased to 72% by continued treatment in the cold. While the compd. differs but slightly from that obtained by **S**. from crude bromopicrotoxinin, the decompn. point was lower (208°) but rises to 225°, however, when prepd. in anhydrous condition from EtOAc. It appears therefore that **S**. actually prepd. a deriv. of **B**, overlooking **A** which remained in the mother liquor. The effect of gaseous HCl on **B** in AcOH was studied in an attempt to prep., under exclusion of  $H_2O$ , one or both the compds.  $C_{15}H_{15}ClBrO_6$  and  $C_{15}H_{17}Cl_2BrO_6$ , and therefrom hydro- $\beta$ -bromopicrotoxininic acid. No such product could be isolated, however. **A** behaves like **B** with respect to the addition of 2 mols. of  $H_2O$ , and yields hydroxy- $\alpha$ -bromopicrotoxininic acid, which differs from the corresponding  $\beta$ -compd. in physical properties. The action of HBr in the cold on **B** is even more energetic than that of HCl, but the yield of new derivs. is considerably smaller. Oxidation of **A** and **B** with  $HNO_3$  leads as in the treatment with coned. HCl and HBr to the formation of derivs. having the same general formula but differing as to m. p. and specific rotation. On treating the  $H_2O$ -addition product of **B**, hydroxy- $\beta$ -bromopicrotoxininic acid, with  $HNO_3$ ,  $\beta$ -bromopicrotoxinindicarboxylic acid,  $C_{15}H_{13}BrO_7 \cdot 2H_2O$ , was obtained. In the replacement of Br in both the  $\alpha$ - and  $\beta$ -forms of hydroxybromopicrotoxininic acid with H, only one product was obtained, a substance having the compn.,  $C_{15}H_{15}O_7$ , and designated picrotoxinin lactone. Hydrobromo- $\beta$ -bromopicrotoxininic acid,  $C_{15}H_{13}Br_2O_7$ , on the other hand, yielded under like treatment the monobasic dihydro- $\beta$ -picrotoxininic acid,  $C_{15}H_{13}O_7$ . The following schematic arrangement indicates in some degree the effects of halogenation on the formation of isomers, as also the relationship of the principal derivs. of picrotoxinin studied. Detailed descriptions are given of the procedures followed in prep. certain



of the picrotoxinin derivs., notably **A** and **B**,  $C_{15}H_{15}BrO_6$ , m. 280° and 290°, resp.; hydroxy- $\beta$ -bromopicrotoxininic acid,  $C_{15}H_{13}BrO_7$ , cubical crystals, m. 208° (225° from EtOAc) (decompn.) (methyl ester,  $C_{16}H_{17}BrO_8 \cdot H_2O$ , m. 220°; ethyl ester,  $C_{17}H_{19}BrO_8 \cdot 3H_2O$ , m. 230° (decompn.)); hydroxy- $\alpha$ -bromopicrotoxininic acid,  $C_{15}H_{13}BrO_7$ , m. 228° (decompn.); hydrobromo- $\beta$ -bromopicrotoxininic acid,  $C_{15}H_{13}Br_2O_7$ , m. 278° (decompn.);  $\beta$ -bromopicrotoxinindicarboxylic acid,  $C_{15}H_{13}BrO_7 \cdot 2H_2O$ , m. 184° (decompn.);  $\alpha$ -bromopicrotoxinindicarboxylic acid,  $C_{15}H_{13}BrO_7 \cdot 4H_2O$ , m. 170° (decompn.); picrotoxinin lactone,  $C_{15}H_{15}O_7 \cdot H_2O$ , m. 298° (decompn.); dihydro- $\beta$ -picrotoxininic acid,  $C_{15}H_{13}O_7 \cdot H_2O$ , m. 210° (decompn.) (ethyl ester,  $C_{17}H_{19}O_7 \cdot H_2O$ , m. 180° (decompn.)).

W. O. E.

**Thiophene series. X. Preparation and reduction of thienyl ketones.** WILHELM STEINKOPF AND ILSE SCHUBART. Dresden. *Ann.* 424, 1-23 (1921); cf. *C. A.* 11, 2327.—2-Propiothienone,  $C_7H_6OS$ , by heating 92 g.  $C_6H_6S$ , 100 g. EtCOCl and 2.8 g.  $P_2O_5$  for 10-12 hrs., finally at 210°, pale yellow oil,  $b_D$  100-1°. Semicarbazone,  $C_8H_{11}ON_3S$ , glistening needles, m. 167°. Aminoguanidine compound,  $C_8H_{12}N_3S$ , pptd. as the picrate,  $C_{10}H_{14}O_7N_3S$ , yellow needles, m. 215°. 2-Butyrothienone,  $C_8H_8OS$ , from 30 g.  $C_6H_6S$ , 120 g. PrCOCl and 0.3-0.4 g.  $P_2O_5$ ,  $b_D$  118-21°. Oxime, needles, m. 57°. Semicarbazone, compact needles, m. 176-6.5°. 2-Isocaprothienone,  $C_9H_{10}OS$ ,  $b_D$  130.5-



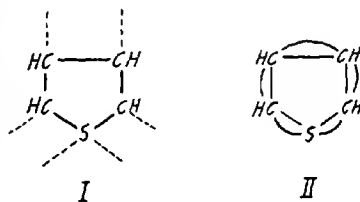
35°. *Oxime*,  $C_8H_{11}ONS$ , m. 88°. An isomeric oxime, m. 102°, was obtained\* in 1 expt. *Semicarbazone*,  $C_{10}H_{13}ON_3S$ , needles, m. 168-9°. *Aminoguanidine compound*,  $C_{10}H_{13}N_4S$ , isolated as the *picrate*, yellow crystals, m. 212°. The free base, pale yellow, m. 98-9°. *p-Phenetidine*, by heating equimol. amts. of the components for 3 hrs. at 190-260°, yellow-brown glistening crystals, m. 51-3°. 5-Methyl-2-acetothienone may be prepd. by the same reaction: 15 g. 2-thiitolene, 13 g.  $AcCl$  and 0.3 g.  $P_2O_5$ , heated 6 hrs., gave 7 g. product, b. 231-2°, m. 27-8°. *Semicarbazone*, m. 225°. This reaction may be used for detecting 2-thiitolene in a mixt. with  $C_7H_8$ . 5-Propyl-2-acetothienone,  $C_8H_{13}OS$ , b<sub>11</sub> 125-6°. *Oxime*,  $C_9H_{15}ONS$ , m. 57°. 2,5-Dimethyl-3-acetothienone,  $C_8H_{13}OS$ , from 12 g. 2,5-thioxene, 11 g.  $AcCl$  and 0.2 g.  $P_2O_5$ , b<sub>11</sub> 126-6°; yield, 1.5 g. *Semicarbazone*,  $C_9H_{15}ON_3S$ , needles, m. 213°. Phenyl 2-thienyl ketone was prepd. by the reaction of 15 g.  $C_6H_5S$ , 50 g.  $Bz_2O$  and 1 g.  $P_2O_5$ . The ketones may be reduced by the action of amalgamated Zn and HCl in the proportion 15 g. ketone, 75 g. Zn and 200 cc. HCl, by gentle warming for 16-20 hrs. Yield of 2-ethylthiophene, 34%, of 2-propylthiophene, 28%. 2-Isomylthiophene,  $C_8H_{11}S$ , b<sub>11</sub> 74-5°; yield, 32%. 2-Methyl-5-ethylthiophene,  $C_7H_{11}S$ , b<sub>11</sub> 53-5°. Phenyl 2-thienylmethane,  $C_{11}H_{11}S$ , from Ph thienyl ketone, by reducing for 30-40 hrs., b<sub>10</sub> 129-35°; yield 15%. *o-Tolyl-2-thienylmethane*,  $C_{12}H_{13}S$ , b<sub>11</sub> 142°; yield, 35%. XI. Thiophene mercury compounds. WILHELM STERNKOPF. *Ibid* 23-61.—This work was undertaken with the idea of detg. how far the Hg compds. can be used in the study of the constitution of thiophene derivs. The present work has shown that the HgCl reaction may be used to differentiate the compd. with free  $\alpha$ -positions and that which is partially or entirely replaced by alkyl groups. Derivs. with 2 free  $\alpha$ -positions yield a mixt. of alc.-sol. and -insol. di-HgCl compds., while if the  $\alpha$ -position is substituted, only alc.-sol. mono-HgCl compds. are formed. 2-Thiophenemercury thiocyanate,  $C_4H_3NS_2Hg$ , by adding a soln. of 0.8 g. NaSCN in 15 cc.  $Me_2CO$  to 3.18 g. 2- $C_4H_3S$  in 75 cc.  $Me_2CO$ , glistening leaflets from  $C_7H_8$ , m. 179-80°. It also results from 2 g.  $Hg(C_4H_3S)_2$  and 1.8 g. HgSCN. The action of 2 mols. NaSCN upon  $C_4H_3S_2HgCl$  gives 2,2'- $Hg(C_4H_3S)_2$ . 2-Chlorothiophene-5-mercury thiocyanate,  $C_4H_2NClS_2Hg$ , glistening leaflets, m. 187°. 2-Bromo derivative,  $C_4H_2NBrS_2Hg$ , small crystals, m. 187-8°. The action of 2 mols. NaSCN gave 5,5'-dibromo-2,2'-mercury dithienyl,  $C_8H_2Br_2S_4Hg$ , m. 181-2°. Di-iodo derivative,  $C_8H_2I_2S_4Hg$ , m. 244-5°. With HgSCN this yields 2-iodothiophene-5-mercury thiocyanate, crystals from  $MeNO_2$ , m. 173°. 5,5-Dimethyl-2,2'-mercury dithienyl,  $C_{10}H_{12}S_4Hg$ , needles, m. 162-2.5°. 2-Thiitolene-5-mercury thiocyanate,  $C_6H_5NS_2Hg$ , microcryst. compd., m. 202-4°. If HgBr is used, 2-thiitolene-5-mercury bromide is obtained, needles, m. 179-80°. In the same way HgI gives the 5-mercury iodide,  $C_6H_5ISHg$ , glistening needles, m. 111-2°. 3-Thiitolene-mercury thiocyanate,  $C_6H_5NS_2Hg$ , decomp. 169°. 2-Ethylthiophene-5-mercury chloride,  $C_6H_5SCHg$ , from 295 g.  $HgCl_2$ , 60 g. 33%  $AcONa$  soln. and 525 cc. alc. containing 4 g. 2-ethylthiophene, m. 147-8°. The constitution was established by transforming it into 5-ethyl-2-acetothienone. 2-Ethylthiophene-5-mercury iodide,  $C_6H_5SIHg$ , glistening needles, m. 96-7°. 5-Mercury thiocyanate,  $C_4H_3NS_2Hg$ , small leaflets, m. 167.5-9°. 2,3-Thioxene-5-mercurous chloride, from 2 g. 2,3-thioxene, 140 g.  $HgCl_2$ , 30 g.  $AcONa$  and 140 g. alc., m. 213-4°. 5-Mercury thiocyanate,  $C_4H_3NS_2Hg$ , felt-like needles, begins to m. 200-2°, but not completely m. at 240°. Hydroxydihydro-2,4-thioxenemercury chloride-mercuric chloride addition product,  $HOCMe.CH:CMc.SCHHgCl.HgCl_2$ , by mixing 3.6 g. 2,4-thioxene, 264 g.

$HgCl_2$ , 54 g.  $AcONa$  soln. and 240 g. alc., felt-like crystals, m. 167-8°; heated with alc. for some time it forms 2,4-thioxene-5-mercury chloride, m. 138-9°. 2,4,2',4'-Tetra-methyl-5,5'-mercury dithienyl,  $C_{11}H_{12}S_4Hg$ , from the above chloride with over 2 mols. NaSCN, glistening leaflets, m. 160-1°. With HgI this gives 2,4-thioxene-5-mercury



iodide, glistening crystals, m. 137–9°. 5-Mercury thiocyanate,  $C_5H_7NS_2Hg$ , m. 173–5°. 2,5-Thiozene-3-mercury thiocyanate,  $C_5H_7NS_3Hg$ , m. 177–7.5°. 3,4-Thiozene-2-mercury thiocyanate, by the use of 2 mols. NaSCN, m. 178–9°. 2-Propylthiophene-5-mercury chloride,  $C_7H_9SClHg$ , m. 155°. 5-Mercury thiocyanate, glistening leaflets, m. 169–9.5°. 5,5'-Dipropyl-2,2'-mercury dithienyl,  $C_{11}H_{15}S_2Hg$ , glistening crystals, m. 57–8°. 2-Isoamylthiophene-5-mercury chloride,  $C_{11}H_{15}SClHg$ , from 2 g. isoamylthiophene, 160 g.  $HgCl_2$ , 32 g.  $AcONa$  soln., and 500 cc. alc., felt-like needles in 75% yield after 9 days' standing, m. 171.5–2°. 5-Mercury thiocyanate,  $C_{10}H_{13}NS_2Hg$ , glistening crystals, m. 194–5.5°. 5,5'-Diisoamyl-2,2'-mercury dithienyl,  $C_{13}H_{19}S_2Hg$ , from 2 g. of the  $HgCl_2$  deriv. and 1.7 g. NaI in 80 cc.  $AcMe$ , m. 55–7°. 2-Benzylthiophene-5-mercury chloride,  $C_{11}H_9SClHg$ , small crystals, m. 189–91°. With NaSCN or NaI, 2,2'-dibenzyl-5,5'-mercury dithienyl,  $C_{22}H_{19}S_2Hg$ , is formed, m. 209–10°. The thiocyanate could not be prepd. 2,5-Diphenylthiophene-3-mercury chloride,  $C_{18}H_{11}SClHg$ , by allowing the components to stand 2 days at room temp., or by boiling for 2.5 hrs., glistening needles, m. 221–2°. The 2,5-diphenylthiophenes m. 152° or 119° give the same product. By boiling with dil. HCl for 0.5 hr., the thiophene is obtained, m. 124–5°. 2,5,2',5'-Tetraphenyl-3,3'-mercury dithienyl, by the action of NaSCN or NaI, prismatic needles. When this is boiled with  $Hg(SCN)_2$ , 2,5-diphenylthiophene-3-mercury thiocyanate,  $C_{17}H_{11}NS_2Hg$ , results, darkens at 200°, does not m. 265°. Ethyl mercury thiocyanate,  $EtHgSCN$ , from 5.2 g.  $EtHgCl$  in 120 cc.  $Me_2CO$  and 1.6 g. NaSCN in 30 cc.  $Me_2CO$ , glistening leaflets, m. 131–1.5°. Phenylmercury thiocyanate,  $PhHgSCN$ , leaflets, m. 232°. It also results by boiling  $Ph_2Hg$  and  $Hg(SCN)_2$ . XII. Chlorination and bromination of thiophene with acetochloro- or bromoamide. WILHELM STEINKOPF AND ANNEMARIE OTTO. *Ibid* 61–71.—Since the prepn. of halogenated thiophenes is so important for thiophene chemistry, the method of Wohl (C. A. 13, 1588) was applied to  $C_4H_4S$ . 2- $C_4H_3S$  was obtained in 33% yield by the action of 1 mol.  $AcNHCl$  at 60°. 3 mols.  $AcNHCl$ , under similar conditions, gave a difficultly separable mixt. of  $C_4H_3S$  and  $C_4H_2S$ , from which only 18% pure  $C_4H_3S$  could be isolated. 1 mol.  $AcNHBr$  and 3 mols.  $C_4H_4S$  gave 52%  $C_4H_3SBr$ . The excess  $C_4H_4S$  is necessary to prevent the formation of  $C_4H_2SBr_2$ , which is obtained in 65% yield by the action of 2.5 mols.  $AcNHBr$  upon 1 mol.  $C_4H_4S$ . 2 mols.  $AcNHBr$  gave only 31%.  $PhNHBr$  gave a smaller yield. The methods are therefore no better than the ones already known. Theoretical considerations and the application of Thiele's theory of partial valences to  $C_4H_4S$  leads to formula I and since neighboring partial valences combine to inactive double bonds, formula II represents a completely satd. thiophene.

C. J. WEST



**Benzocoumarones.** K. FRIES AND R. FRELLSTEDT. *Techn. Hochschule Braunschweig. Ber.* 54B, 715–25 (1921).—F. and R. hope to find among derivs. of oxindigo obtained by substitution in the  $C_6H_4$  nucleus compds. whose heterocyclic ring is less easily ruptured hydrolytically than that of the mother substance; such compds., they believe, it will be possible to convert into vat dyes without decompn.  $\beta$ -Naphthyl chloroacetate (140 g. from 144 g.  $\beta$ -naphthol gently boiled with 113 g.  $ClCH_2COCl$  until the evolution of HCl ceased—about 3 hrs.), needles from  $AcOH$ , m. 96°; 22 g. in 90 cc.  $CS_2$ , heated 1 hr. on the  $H_2O$  bath with 27 g.  $AlCl_3$ , freed from the  $CS_2$ , heated 4 hrs. at 120° and distd. with steam, gives about 20% 4,5-benzo-3-coumarone (A), needles

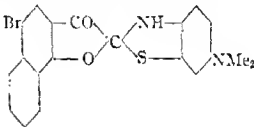


from benzene, m. 133°, sol. in concd.  $\text{H}_2\text{SO}_4$  with faintly yellow color, slowly sol. in dil.  $\text{NaOH}$ , quickly in the presence of alc., with bluish red color, gives with boiling  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  3-acetoxy-4,5-benzocoumarone, needles from alc., m. 85°, while 1.8 g. of the A and 1.5 g.  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  in boiling alc. slowly treated with 1 cc. fuming  $\text{HCl}$  and boiled until the ppt. no longer increases in amt. yields the 2-p-nitrobenzal derivative, yellow needles from  $\text{C}_6\text{H}_6$ , m. 270°, sol. in concd.  $\text{H}_2\text{SO}_4$  with red color, stable towards boiling  $\text{NaOH}$ . 4,5-Benzo-2,3-coumarandione 2-p-dimethylaminoanil (2.5 g. from 1.5 g.  $p\text{-ONC}_6\text{H}_4\text{NMe}_2$  in 30 cc. alc. at 0° treated with 1.5 cc. of 2 N  $\text{KOH}$  and then with 1.84 g. A in 20 cc. alc., removed from the cooling bath in about 10 min. and, as soon as room temp. has been reached, treated within the course of 15 min. with 7 cc.  $\text{H}_2\text{O}$ , filtered and washed with alc. until the washings are light red), red needles with blue-black surface luster from  $\text{C}_6\text{H}_6$ , m. 231°, easily sol. in dil.  $\text{NaOH}$  in the presence of a little alc., reprecipitated by  $\text{AcOH}$ , sol. in much  $\text{AcOH}$ , sol. in concd.  $\text{H}_2\text{SO}_4$  with red-brown color,  $\text{H}_2\text{O}$  pptg. the yellow dione; all attempts to add A to the anil (cf. C. I. 5, 1431) and thus obtain the oxindigo failed, the anil being recovered unchanged. 4,5-Benzo-2,3-coumarandione, from 1 part of the anil in 3 parts concd.  $\text{H}_2\text{SO}_4$  treated with  $\text{H}_2\text{O}$ , orange-yellow needles from  $\text{C}_6\text{H}_6$ , m. 182° (decompn.), only slowly hydrolyzed by cold dil. soda, quickly on boiling and reprecipitated from the yellow soln. by  $\text{HCl}$ , easily sol. in concd.  $\text{H}_2\text{SO}_4$  with blood-red color becoming colorless on heating, easily reacts with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ . The extraordinary stability of this lactone towards dil. soda as compared with 2,3-coumarandione shows the marked influence of the "side chain" on the stability of the heterocyclic ring and leads to the hope that 4,5,4',5'-dibenzoxindigo, whose synthesis F. and F. have not yet been able to effect, will be one of the oxindigo derivs. which can be converted into vat dyes without decompn. 4,6-Dibromo-2-aceto-1-naphthol, from 18.6 g. 1,2-C<sub>10</sub>H<sub>6</sub>(OH)Ac in 120 cc.  $\text{CHCl}_3$  and 32 g. Br in 60 cc.  $\text{CHCl}_3$ , yellow needles or prisms from  $\text{AcOH}$ , m. 147° (decompn.), quickly changed by dil.  $\text{NaOH}$  on warming or adding alc. with formation of a nonhomogeneous brown-red product, sol. in  $\text{H}_2\text{SO}_4$  with orange color and reprecipitated by  $\text{H}_2\text{O}$ ; 34.1 g. in 150 cc. alc. boiled with 24.2 g.  $\text{PhNMe}_2$  until completely dissolved (10-2 min.), faintly acidified and pptd. with  $\text{H}_2\text{O}$ , gives 26 g. 5-bromo-6,7-benzo-3-coumaranone (B) yellowish needles or lancelets from alc.; m. 158°, only slowly attacked by dil. alkalis, more quickly in the presence of alc., the soln. gradually becoming red; p-nitrobenzal derivative, from 0.5 g. B and 0.4 g.  $o\text{-NC}_6\text{H}_4\text{CHO}$  in 30 cc. boiling alc. treated with 2 cc. fuming  $\text{HCl}$ , yellow needles from xylene, m. 335°, not attacked by aq. alkalis; in contact with concd.  $\text{H}_2\text{SO}_4$  the crystals become deep red, the soln. yellow; terephthalal derivative, similarly prepd. but in  $\text{AcOH}$  as the solvent, yellow needles from  $\text{PhNO}_2$ , m. 311° (decompn.), stable towards aq. alkalis, sol. in  $\text{H}_2\text{SO}_4$  with brown-red color. 5-Bromo-6,7-benzo-2,3-coumaranone 2-p-dimethylaminoanil, stout dark red needles with steel-blue surface luster from  $\text{C}_6\text{H}_6$ , m. 251°, sol. in  $\text{H}_2\text{SO}_4$  with red-brown color,  $\text{H}_2\text{O}$  pptg. the compd. C below. Many attempts were made to add B to the anil, a few times successfully, but the proper conditions have not been detd. with certainty. Thus, in 2 cases, 0.5 g. of the anil and 0.35 g. B gently boiled 15 hrs. in 25 cc.  $\text{C}_6\text{H}_6$  and allowed to stand a long time yielded a small amt. of red-brown crystals, containing N, m. 246°, easily sol. in dil.  $\text{NaOH}$ , reprecipitated by  $\text{AcOH}$ , dissolves when treated in  $\text{AcOH}$  with a few drops of fuming  $\text{HCl}$  but the yellow soln. soon deposits an orange substance quite stable towards  $\text{NaOH}$ , free from N, sol. in  $\text{H}_2\text{SO}_4$  with cherry-red color, seps. from  $\text{PhNO}_2$  in stout orange needles with golden luster, does not m. 350°, sublimes when cautiously heated; the method of formation and its behavior indicate that it is 5,5'-dibromo-6,6',7',7'-dibenzoxindigo, but not enough was obtained for analysis. 2-Terephthalal derivative of B, from 1 g. B in 30 cc.  $\text{AcOH}$  slowly treated with 1 g. more  $\text{NaNO}_2$  and, after 5 hrs., again treated with 1 g. more  $\text{NaNO}_2$  and allowed to stand overnight, yield.



varying but good), yellow needles from AcOH, m.  $207^{\circ}$  (decompn.), sol. in  $\text{H}_2\text{SO}_4$  with red color, repptd. by  $\text{H}_2\text{O}$ ; 2 g. in 30 cc. AcOH boiled until dissolved with 10 cc. fuming HCl and poured into  $\text{H}_2\text{O}$  gives 1.1 g. 2-[1-hydroxy-4-bromonaphthoyl]formic acid (C), yellow needles from  $\text{C}_6\text{H}_6$ , m.  $168^{\circ}$  (decompn.), gives the indophenin reaction with  $\text{C}_6\text{H}_6$  containing thiophene. C is also obtained in 50% yield from the anil above in 5 parts concd.  $\text{H}_2\text{SO}_4$  poured into 10 parts  $\text{H}_2\text{O}$ ; 1 g. with 0.9 g. B in 10 cc. warm AcOH treated with 6 cc.  $\text{H}_2\text{SO}_4$  yields 2,3'-bis-[5-bromo-6,7-benzocoumaran]indigo, stout brown-red needles from  $\text{PhNO}_2$ , m.  $348-50^{\circ}$ , sol. in  $\text{H}_2\text{SO}_4$  with red color, repptd. by  $\text{H}_2\text{O}$ , only slowly attacked by aq. alkalis but dissolves in the presence of alc. with blue color, cannot be converted into a vat dye without decompn. 2-[5-Bromo-6,7-benzocoumaran]-3'-indoleindigo, from isatin and B, fine red needles from  $\text{PhNO}_2$ , m.  $300^{\circ}$  (decompn.), sol. in  $\text{H}_2\text{SO}_4$  with wine-red, in NaOH in the presence of alc. with yellow color, is not regenerated from the  $\text{Na}_2\text{S}_2\text{O}_4$  vat. 2-p-Dimethylaminoandino-2-mercapto-5-bromo-6,7-benzo-3-coumarone, from 1 g. of the above anil in 50 cc.  $\text{C}_6\text{H}_6$  at  $70-80^{\circ}$  treated 12 hrs. with dry  $\text{H}_2\text{S}$ , red needles from  $\text{C}_6\text{H}_6$ -benzine (yield, 0.9 g.), m.  $176^{\circ}$  (decompn.), sol. in  $\text{H}_2\text{SO}_4$  with brown-red, in alkalis in the presence of alc. with yellow color; 1 g. in 20 parts  $\text{H}_2\text{O}$ , 5 parts alc. and 2 cc. of 2 N KOH slowly treated with 0.8

g.  $\text{K}_2\text{Fe}(\text{CN})_6$  in  $\text{H}_2\text{O}$  gives 0.8 g. of the spiran



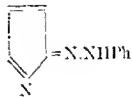
red needles from  $\text{PhNO}_2$ , m.  $260^{\circ}$  (decompn.), sol. in  $\text{H}_2\text{SO}_4$  with violet color.

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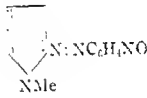
**Azopyrroles. I.** R. CUSA. Univ. Bologna. *Gazz. chim. Ital.* 51, I, 40-55 (1921).—The azopyrroles through analogy of the pyrroles with the phenols and with  $\text{PhNH}_2$  are comparable to the hydroxyazo and aminoazo compds. since the azopyrroles may be considered as having 2 forms, one azoic (I) and the other pyrrolic-lydrazonic (II). Plancher concluded that I is the proper formula for



I



II



III

the free compds. and II is correct for the compds. with acids, mainly on the basis of their behavior toward  $\text{PhNC}$ . The results here described were intended to establish whether there is any isomorphism between pyrroleazobenzene and  $\text{PhN:NPh}$  and to det. the constitution of these compds. by spectrographic studies. F. p. detns. with  $\text{PhN:NPh}$  as the solvent showed anomalies that indicate that pyrroleazobenzene gives solid solns. with this solvent. This result conforms with the fact that pyrrole gives solid solns. with  $\text{C}_6\text{H}_6$ . A comparison of the absorption spectra (visible part) of pyrroleazobenzene, pyrroleazo-*o*-nitrobenzene, the *m*- and *p*-isomers and *N*-methylpyrroleazo-*p*-nitrobenzene (III) showed that the curves are all similar to that of III, which necessarily has the azoid constitution. From this it is concluded that all these derivs., even in the solid state, have the azoid constitution of I. Crystallographic detns. on pyrroleazobenzene and  $\text{PhN:NPh}$  show no analogies. The alkali salts of these compds. except III, however, have the constitution of II, since their  $\text{Me}_2\text{CO}$  solns. undergo sharp color changes on adding EtOK with formation of the corresponding



nitronic acid salt. **III** has no labile H and so remains unchanged. One g. pyrrole in EtOH + 5 g. NaOAc in concd. aq. soln. treated at 0° slowly with  $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2\text{Cl}$  (from 2 g.  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ ) gave a brown ppt. of *p*-nitrobenzenesazopyrrole, orange crystals from ligroin, m. 148-9°. The *m*-deriv. similarly prepd. gave bright yellow needles, m. 91-2°. The *o*-deriv. gave orange-yellow needles, m. 121-2°. *N*-Methylpyrrole similarly treated with  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$  gave *p*-nitrobenzenesazo-*N*-methylpyrrole as violet scales. E. J. WITZEMANN

**The color of the indigoids.** J. MARTINET. *Rev. gén. mat. col.* **25**, 17-8(1921).—In spite of the accumulated evidence with regard to the relation between color and chem. constitution of compds., it is still impossible to express this relationship in a general manner by a mathematical formula, and to calc. selective absorption. Certain rules, however, permit the color of org. compds. to be predicted with reasonable probability, as may be demonstrated in the case of the indigoids. Thus there is an increase in the depth of color in passing from brownish red isoindigotin (3,3'-bisindole) to violet-red indirubin and blue indigotin; a similar relationship exists in the case of oxindigo (2,2'-bisoxymarone), thioindigo (2,2'-bisoxythionaphthene) and indigotin; substituents in the 6,6'-positions, such as Me, HO, NH<sub>2</sub>, and the halogens, lessen the depth of color. Facts such as these are not isolated cases, and could be predicted by the application of the following rules: (a) The union of an auxochrome and a chromophore by means of a chain of conjugated double bonds between C leads to an increase in the depth of color (bathochromic effect). (b) The direct union of a chromophore and an auxochrome decreases the depth of color (hypsochromic effect). This first rule arises from the examn. of a large number of compds. of established constitution, but the second is less well known. For example, the group NO is a powerful chromophore, and NHEt is a powerful auxochrome. When these groups are united by a benzene ring the deeply colored  $p\text{-ONC}_6\text{H}_4\text{NHEt}$  results (a), whereas when these groups are directly united the almost colorless PhN(NO)Et results (b). In the case of isoindigotin, the auxochrome NH groups being directly attached to the chromophore, CO groups are in an unfavorable position for the production of color, while in indigotin the NH group exerts its max. effect because it is attached to the CO group by a benzene nucleus on one side, and by a C atom, which forms part of a chain with double conjugated bonds, on the other. The formula of indirubin occupies an intermediate position between the two, and this fact is reflected in its color. The increase in the depth of color in passing from oxindigo to thioindigo and indigotin is a bathochromic effect due to the increasing power of the auxochromes OPh—, SPh—, NHPh—, and is in agreement with known facts in other series. With regard to the diminution in the depth of color produced by the introduction of auxochromes in positions 6,6', it appears that (c) the effect of two auxochromes is cumulative when in the *p*-position, but that they act in contrary directions when in the *m*-position with respect to one another. This also is in agreement with experience in other series; thus *o*-nitro-*p*-phenylenediamine is greenish black, while *o*-nitro-*m*-phenylenediamine is yellowish red, and nitroquinol is red while *asym*-nitroresorcinol is lemon-yellow in color. This rule is particularly well exemplified in the indigoid series, for all 5,5'-derivs. are considerably deeper in color than the corresponding 6,6'-derivs. The application of these 3 rules serves as an excellent guide in the search for new coloring matters of a desired shade.

J. C. S.

**Remarks on some earlier communications.** F. KEHRMANN. Univ. Lausanne. *Ber.* **54B**, 657-9(1921).—Brief replies to the criticisms of v. Braun on the constitution of pyronine (*C. A.* **13**, 1322) and of Hantzsch on absorption spectra of triphenylmethane dyes (*C. A.* **13**, 2524) and comments on the conclusions of Dilthey on pyrylium compds. (*C. A.* **14**, 2641).

CHAS. A. ROUELLER



**Mitragynine** and **mitraversine**, two new alkaloids from species of **Mitragyne**. ELLEN FIELD. Univ. Edinburgh. *J. Chem. Soc.* 119, 887-91 (1921).—**Mitragyne speciosa**, extd. with alc., the alc. residue dissolved in AcOH and dild. to ppt. resin and chlorophyll and then made alk. with  $\text{NH}_4\text{OH}$ , gave an amorphous ppt., from an AcOH soln. of which picric acid ppts. **mitragynine picrate**,  $\text{C}_{27}\text{H}_{34}\text{O}_4\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , orange-red slender needles from glacial AcOH, or MeOH, m. 223-4°. **Mitragynine**, amorphous crystals, b<sub>1</sub> 230-40°, m. 102-6°, contains 3 MeO groups. **Hydrochloride**, rhombic leaflets from alc.-Et<sub>2</sub>O, m. 243°. **Acetate**, slender silky needles from AcOH-Et<sub>2</sub>O, m. 142°. **Trichloroacetate**,  $\text{C}_{27}\text{H}_{31}\text{O}_5\text{N}_2\cdot\text{CCl}_3\text{CO}_2\text{H}$ , needles from  $\text{Me}_2\text{CO-Et}_2\text{O}$ , m. 157°. The hydrolysis product of the acetate with EtONa is a **dicarboxylic acid**,  $\text{C}_{17}\text{H}_{22}\text{N}(\text{OMe})-(\text{CO}_2\text{H})_2$ , m. 280°. Distd. with CaO, a green oil was obtained from which a red **picrate** was prepd., m. 218°. **Mitragynine** may be a deriv. of indole or at least undergoes decompn. with the formation of such a substance. **M. diversifolia**, treated with alc. and AcOH as above, the AcOH soln. poured into H<sub>2</sub>O, made alk., extd. with Et<sub>2</sub>O, the Et<sub>2</sub>O extd. with 10% AcOH and this ext. made alk. gave 0.27% of the wt. of the leaves of **mitraversine**,  $\text{C}_{27}\text{H}_{34}\text{O}_4\text{N}_2$ , m. 237°. It contains 2 MeO groups. **Hydrochloride**, rhombic leaflets, m. 208-10°.

C. J. WEST

**New degradation product of physostigmine**. EDGAR STEEDMAN. Univ. Edinburgh. *J. Chem. Soc.* 119, 891-4 (1921).—1 g. eseroline methiodide boiled with 13 cc. of EtONa (0.5 g. Na in 50 cc. EtOH) and excess of MeI for 1.5 hrs. in a stream of H<sub>2</sub>, gave 0.3 g. of a compound  $\text{C}_{10}\text{H}_{17}\text{ON}_2\text{I}$  (net loss of  $\text{C}_6\text{H}_5$ ), plates from MeOH, darkens 210°, m. 235° (decompn.). It contains 3 Me groups of which 1 may be MeO. The I is easily removed with moist Ag<sub>2</sub>O. The distn. of this quaternary base gave a volatile amine, as yet not identified.

C. J. WEST

**Synthesis of homomorpholine and of benzohomomorpholine**. JULIUS V. BRAUN AND OTTO BRAUNSDORF. Landw. Hochschule Berlin. *Ber.* 54B, 685-703 (1921).—In the synthesis of these 2 new compds. v. B. and B. followed in part the course pursued by Knorr in synthesizing morpholine and benzomorpholine, using  $\text{Br}(\text{CH}_2)_3\text{OBz}$  (A) to introduce the  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$  part of the ring, while K. used ethylene oxide to introduce  $-\text{CH}_2\text{CH}_2\text{O}-$  (*Ann.* 301, 1 (1898)). It was first tried to accomplish the synthesis by the following series of reactions:  $\text{A} + \text{NH}_3 \rightarrow \text{H}_2\text{N}(\text{CH}_2)_3\text{OBz} + \text{CH}_2\text{CH}_2\text{O} \rightarrow \text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{OBz} \rightarrow \text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{OH} \rightarrow$

$\text{NH} < \begin{smallmatrix} \text{CH}_2\text{CH}_2\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{smallmatrix} > \text{O}$  (B), but, working in HO-free solvents, best in  $\text{C}_6\text{H}_6$  at 100°, there

was obtained from A and  $\text{NH}_3$ , even with an excess of the latter, together with a product of quaternary character, a mixt. of bases boiling within a large range from which, to be sure, could be isolated a fraction b<sub>1</sub> about 150° and having approx. the compn. of  $\text{H}_2\text{N}(\text{CH}_2)_3\text{OBz}$  but extraordinarily small in amt. Next it was tried to carry out the following reactions:  $\text{A} + \text{NH}_2\text{Me} \rightarrow \text{MeNH}(\text{CH}_2)_3\text{OBz} \rightarrow \text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{OBz} \rightarrow \text{BzO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{OBz} \rightarrow \text{BzO}(\text{CH}_2)_2\text{N}(\text{CH}_2)_3\text{OBz} \rightarrow \text{B}_2$ , but when 2.5 mols.  $\text{MeNH}_2$  in 7%  $\text{C}_6\text{H}_6$  soln. was heated 7 hrs. at 100° with 1 mol. A in a sealed tube, then treated with H<sub>2</sub>O and dild. acid, extd. with Et<sub>2</sub>O, made alk. and fractionated there were obtained chiefly 2 fractions: (1) The hoped-for  $\gamma$ -methylaminopropyl benzoate, b<sub>10</sub> 144-5°, as an oil with a strongly basic odor but in only very small amt. (2 g. from 50 g. A); (2) di-[ $\gamma$ -benzyloxypropyl]methylamine, very viscous oil of faintly basic odor, b<sub>4</sub> 268-72°, in much greater yield (12 g.); its **hydrochloride**, silvery, non-hygroscopic leaflets from EtOH-Et<sub>2</sub>O, m. 137°, the **chloroaurate** and **chloroplatinate** are oily; **methiodide**, crystals from alc., m. 187°; the base boiled 1.5 hrs. in aq. alc. with 8-10 mols. NaOH, acidified, freed from the alc. by distn. and from the BzOH with Et<sub>2</sub>O and made alk. gives di- $\gamma$ -hydroxypropylmethylamine, thick oil, b<sub>13</sub> 164-5° (yield, 80%), forming an oily **hydrochloride**, **chloroaurate** and **chloroplatinate** but a solid **picrolonate**, crystals



from EtOH-Et<sub>2</sub>O, m. 136°, and a *methiodide*, needles from alc., m. 110°. The synthesis of **B** was finally effected as follows: When 2 mols. PhNH<sub>2</sub> and 1 mol. **A** are heated 1.5-2.0 hrs. on the H<sub>2</sub>O bath, then dissolved in dil. acid, freed from traces of unchanged **A** with Et<sub>2</sub>O, made alk. and fractionated *in vacuo*, PhNH<sub>2</sub> dists. over below 100°, then the temp. quickly rises and at 270-310° (chiefly 270-80°) there passes over a viscous yellowish fraction, consisting chiefly of *γ*-*anilinepropyl benzoate* (**C**); at the same time there is marked decompn. and a not inconsiderable residue remains behind. Analysis shows that the **C** is not quite pure and redistn. is again accompanied by decompn. It was therefore not attempted to isolate the **C** and the mixt. with PhNH<sub>2</sub> was boiled 1 hr. in aq. alc. with excess of alkali, acidified, freed from the alc. with steam, again made alk., extd. with Et<sub>2</sub>O, dried a short time over fused potash and fractionated, giving 80% of HO(CCl<sub>3</sub>)<sub>2</sub>NHPh (**D**), b<sub>10</sub> 173-80°, d<sub>4</sub><sup>20</sup> 1.073 (cf. Rindfuss and Harnack, *C. A.* 14, 2930); the *nitroso derivative*, *hydrochloride* and *chloroplatinate* are oils; *picrate*, m. about 70°; *picrolonate*, crystals from alc., m. 165°; *quaternary methiodide*, tables from alc., m. 135°. **D** does not react with AcH even after boiling for hrs. in Et<sub>2</sub>O in the presence of potash. The small residue remaining on distg. **D** is *N*-*di-γ*-*hydroxypropyl*aniline, very thick yellowish oil, b<sub>10</sub> about 240-5°, m. 108°. **B** heated in 50% CHCl<sub>3</sub> soln. and a trace of H<sub>2</sub>O with an equiv. amt. of ethylene oxide 6 hrs. at 50° gives almost quant. *N*-*γ*-*hydroxypropyl*-*N*-*β*-*hydroxyethyl*aniline (**E**), very thick oil, b<sub>9</sub> 220-5°, d<sub>4</sub><sup>17</sup> 1.009; *hydrochloride* and *methiodide*, oils; *picrate*, crystals from EtOH-Et<sub>2</sub>O, m. 102°. **E** can be converted into *N*-*phenylhomomorpholine* (**F**) by Knorr's method by intramol. dehydration with H<sub>2</sub>SO<sub>4</sub> but the success of the operation depends upon keeping within very narrow limits of time and temp., 5 parts of 70% H<sub>2</sub>SO<sub>4</sub>, as recommended by K., proved very satisfactory, but the time (8-10 hrs.) given by him is too long and the temp. interval (160-70°) too wide; as soon as the temp. goes beyond 165° extensive resinification becomes apparent and below 160° the reaction is extraordinarily slow; to obtain any considerable yield of **F** the mixt. must be heated at most 6-8 hrs. at 160-5° in a sealed tube; it is then dild. with H<sub>2</sub>O, made alk., distd. with steam and the distillate extd. with Et<sub>2</sub>O, dried and fractionated; the **F** (30% yield) is an oil of unpleasant basic odor, b<sub>9</sub> 155-8°; *hydrochloride*, m. 168-9°; *chloroplatinate*, indistinctly cryst. floccs from H<sub>2</sub>O, decomp. 196-7°; *picrate*, crystals from alc., m. 143°; *picrolonate*, rhombic leaflets from alc., m. 162-3°. **F** can be boiled for hrs. with Ac<sub>2</sub>O without change and it is not affected by CrO<sub>3</sub>-AcOH, both facts indicating that in its formation from **E** the H<sub>2</sub>O split off does not come from one of the OH groups and a H atom attached to C; the indifference towards CrO<sub>3</sub> also indicates that there has not been a shortening of the trimethylene ring with formation of such a compd. as PhN-CH<sub>2</sub>-CH<sub>2</sub>-O-CHMe-CH<sub>2</sub> or PhN-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHMe.

A shortening of the ring to PhN-CHMe-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> or PhN-CH<sub>2</sub>-CH<sub>2</sub>-O-CHMe

is very improbable in view of the great resistance of **F** towards concd. or dil. acids. Like piperidine with aromatic substituents on the N, **F** cannot be ruptured by Hofmann's method. On the H<sub>2</sub>O bath it combines easily with MeI, but the resulting *methiodide* is a non-crystallizable, thick, faintly yellow sirup; the *methochloride* is likewise oily; *chloroplatinate*, fine red-yellow powder, m. 182-3°. The *methiodide* boiled with 50% KOH regenerates **F**. **F** nitrosated in the usual way (keeping the temp. below -10°) and allowed to stand 6 hrs. in ice-NaCl gave almost 50% of *N*-*p*-*nitrosophenylhomomorpholine hydrochloride*, fine red-yellow cryst. mass; free *nitroso base*, green oil, 10 g. of which, boiled 0.5 hr. under a reflux with 400 cc. of aq. NaHSO<sub>3</sub> (d. 1.2), treated with 200 cc. HCl, evapd. to 0.5 its vol., made alk., distd. with steam into dil. HCl, evapd. to dryness, extd. with alc. and pptd. with Et<sub>2</sub>O, gave 2 g. of the *hydrochloride*, fine cryst. powder, m. 174-5°, of *homomorpholine* (**B**), oil of sharp ammoniacal odor,



very difficult to dehydrate completely and therefore not yet obtained pure, fumes in the air, reacts with  $\text{HNO}_3$  without evolution of N but forming an easily sol. NO compd. and gives with the so-called alkaloid reagents characteristic ppts., e. g., reddish brown with  $\text{I}_2\text{-KI}$ , orange-red changing to brownish with  $\text{HgI}_2\text{-KI}$ , yellowish with phosphomolybdic acid, white with  $\text{HgCl}_2$ ; it is stable towards hydrolytic agents, being unattacked when heated several hrs. at  $130^\circ$  in sealed tubes with several vols. of fuming  $\text{HCl}$ , whence it is concluded that when the *p*-nitrosophenyl residue is split off the heterocyclic nucleus in **F** remains intact and is present unchanged in **B**. **B** differs from morpholine in its behavior towards  $\text{H}_2\text{PtCl}_6$ , its soln. becoming green and depositing green flocks. The benzoyl derivative, prepd. by the Schotten-Baumann method, is a thick oil; *p*-nitrobenzoyl derivative, m.  $83\text{--}4^\circ$ . *N*- $\gamma$ -Hydroxypropyl-*o*-anisidine, from 3 mols. *o*-anisidine and 1 mol. **A** heated 2 hrs. on the  $\text{H}_2\text{O}$  bath, then boiled 1 hr. with an excess of aq. alc.  $\text{NaOH}$ , b<sub>10</sub>  $194\text{--}6^\circ$  (yield, 85%), the hydrochloride is extremely hygroscopic, the picrate is oily, the picrolonate m.  $160\text{--}1^\circ$ , the quaternary methiodide, crystals from alc., m.  $163^\circ$ ; the nitroso derivative is oily. The base heated 5 hrs. in a sealed tube at exactly  $160^\circ$  with 4 parts fuming  $\text{HCl}$  yields 80% of the hydrochloride, cryst. powder from  $\text{EtOH-Et}_2\text{O}$ , m.  $168\text{--}70^\circ$ , of *N*- $\gamma$ -propyl-*o*-aminophenol which is freed from the  $\text{HCl}$  salt by treating in  $\text{H}_2\text{O}$  under  $\text{Et}_2\text{O}$  with soda, removing the  $\text{Et}_2\text{O}$  with  $\text{H}$ , drying *in vacuo* in a slow current of  $\text{H}$  at  $50\text{--}60^\circ$ , taking up in  $\text{Et}_2\text{O}$ , pptg. dark impurities with petr. ether and again evapg. in  $\text{H}$ ; it forms an almost colorless cryst. mass, m.  $78\text{--}7^\circ$ , exceedingly unstable in air, especially in the presence of moisture, oxidizing and darkening, decomps. completely on distn., even in a good vacuum, gives a dark red color with  $\text{FeCl}_3$ , dissolves clear in alkalies; nitroso derivative, fine, only faintly colored cryst. powder from  $\text{Et}_2\text{O}$ -petr. ether, m.  $96\text{--}7^\circ$ . When the base is heated about  $0.5$  hr. on the  $\text{H}_2\text{O}$  bath with approx. 1 mol. alkali (if an excess of alkali is used practically the only reaction is an alkylation of the basic N atom by the  $\text{ClCH}_2\text{CH}_2\text{CH}_2$  groups), then treated with more alkali and distd. with steam, most of the product remains behind as a dark mass but there is obtained about 10% of benzohomomorpholine (**G**), b<sub>10</sub>  $150\text{--}60^\circ$ ; picrate, fine cryst. ppt. from  $\text{Et}_2\text{O}$ , darkens above  $160^\circ$ , m.  $190^\circ$ ; quaternary methiodide, long needles from alc., m.  $175\text{--}6^\circ$ . That **G** has really the structure assigned to it and not one of the isomeric structures  $\text{C}_8\text{H}_9\text{O.CH}_2\text{CHMe.NH}$  (**H**) or

$\text{C}_8\text{H}_9\text{O.CHMe.CH}_2\text{NH}$  is shown by the fact that, in the first place, it is different from the

known **H** (Störmer, *Ber.* 31, 752 (1898), and, secondly, when its methiodide above is boiled with 30%  $\text{KOH}$  it yields *o*-dimethylhomophenyl allyl ether, b<sub>10</sub>  $129\text{--}30^\circ$ , which was synthesized from the  $\text{NO}_2$  compd. with  $\text{SnCl}_4$  and  $\text{HCl}$ ; picrate, darkens  $162^\circ$ , m.  $167\text{--}8^\circ$ ; hydrochloride, m.  $182\text{--}3^\circ$ ; phenylthiourea, m.  $117^\circ$ ; quaternary methiodide, m.  $181\text{--}2^\circ$ , smoothly loses  $\text{MeI}$  on heating *in vacuo*, yielding the *N*-dimethyl base, b<sub>10</sub>  $118\text{--}9^\circ$ , whose picrate, needles from  $\text{Et}_2\text{O}$ , m.  $166\text{--}7^\circ$ , hydrochloride is oily and chloroplatinate, ochre-yellow powder, m.  $160\text{--}1^\circ$ . C. A. R.

**Azthionium salts of the naphthalene series.** F. KEHRMANN AND TAKIS CH. CHRISTOPOULOS. Univ. Lausanne. *Ber.* 54B, 649–57 (1921).—The present paper contains further observations made on the azthionium salts prepd. by treating the thio derivs. of  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\text{NHPh}$  and  $\alpha$ - and  $\beta$ -( $\text{C}_{10}\text{H}_7$ ) $\text{NH}$  with oxidizing agents in the presence of strong acids (*Ann.* 322, 44 (1902)). Thiophenyl- $\alpha$ -naphthylamine (**A**), obtained in 40% yield by heating 15 g.  $\alpha$ - $\text{C}_{10}\text{H}_7\text{NHPh}$  and 4 g.  $\text{S}$  8 hrs. at  $210^\circ$  instead of  $240^\circ$  like Kym (*Ber.* 23, 2464 (1890)) and working up the melt through the picrate as previously described, seps. from ligroin in golden yellow tablets, m.  $130.5^\circ$ , forms in alc.,  $\text{C}_2\text{H}_5$ ,  $\text{AcOH}$ , etc., pure yellow solns. with bluish green fluorescence, becomes deep blue with concd.  $\text{H}_2\text{SO}_4$  and a vivid wine-red with a little  $\text{HNO}_3$ . The  $\text{H}_2\text{SO}_4$  soln. evolves much  $\text{SO}_2$ ; if it is dild. with ice  $\text{H}_2\text{O}$  after the evolution of  $\text{SO}_2$  has



ceased, there is obtained at first a clear wine-red soln. of the monoacid azthionium sulfate which, however, soon decomps. in the manner described below; short warming with  $\text{Ac}_2\text{O}$  and a little  $\text{ZnCl}_2$  gives an *acetyl derivative*, colorless crystals from  $\text{C}_6\text{H}_6$ , m.  $132^\circ$ . A in alc. boiled 1 hr. with the necessary amt. of  $\text{H}_2\text{O}_2$  and a little powdered  $\text{NaHCO}_3$  yields the *sulfoxide*,  $\text{C}_{10}\text{H}_8 < \begin{smallmatrix} \text{NH} \\ \text{SO} \end{smallmatrix} > \text{C}_6\text{H}_5$ , cryst. granules from  $\text{EtOH-C}_6\text{H}_6$ ,

decomp. about  $194^\circ$ , forms in concd.  $\text{H}_2\text{SO}_4$  a pure blue soln. changing to red on addition of ice and depositing phenonaphthothiazone; if, on the other hand, it is dild. with ice and at the same time with a considerable excess of 20%  $\text{HClO}_4$  it yields  *$\alpha$ -naphtho-phenazhionium perchlorate*, obtained more easily and in purer form by gradually treating a satd. soln. of A in AcOH with a mixt. of 1 part satd. aq.  $\text{FeCl}_3$  and 2-3 parts AcOH; the soln. at once becomes dark violet-blue and deposits a cryst. magma of dark blue microneedles of an Fe double salt of a quinhydrone-like intermediate oxidation product; in contact with a sufficient excess of the oxidizing soln. this disappears quickly and is replaced by a second crystn. of dark red needles of the Fe salt (B) of the holoquinoid stage. After all the  $\text{FeCl}_3$  has been added, the cryst. magma is treated with much 20%  $\text{HClO}_4$  and slowly dild. with much  $\text{H}_2\text{O}$ ; the Fe salt dissolves with fuchsin-red color but the above perchlorate almost instantly seps. again; it forms dark chocolate-brown needles with violet metallic luster, slightly sol. in cold  $\text{H}_2\text{O}$  with red color and quickly decomps. on heating into phenonaphthothiazone. The above *ferrie chloride double salt* (B),  $\text{C}_{10}\text{H}_8 \cdot \text{NSCl} \cdot \text{FeCl}_3$ , dissolves in cold  $\text{H}_2\text{O}$  with intense fuchsin-red color but in a few min. begins to deposit the thiazone. A *perbromide*, a dark red-brown powder which quickly decomps. at room temp., is obtained quant. from a satd. soln. of A in AcOH treated with an excess of a mixt. of 1 part Br and 2 parts AcOH. The phenonaphthothiazone (designated "phenonaphthazhione" in the earlier paper) is obtained almost quant. when the AcOH soln. of A, completely oxidized with  $\text{FeCl}_3$ , is treated in the presence of a sufficient excess of the oxidizing agent with enough  $\text{H}_2\text{O}$  so that at first everything dissolves with a deep red color; after 24 hrs. the soln. has become colorless and the thiazone has sepd. as a flocculent dark orange ppt. When the above perbromide, while fresh and still moist, is added in small portions to an excess of alc.  $\text{NH}_3$  and acidified after 0.5 hr. with dil.  $\text{HCl}$ , the orange soln., containing a dark flocculent by-product in suspension, becomes intensely cherry-red; the alc. is allowed to evap. at room temp., powdered  $\text{NaCl}$  added, the ppt. washed with a little  $\text{H}_2\text{O}$  until the latter begins to redden, then extd. with boiling  $\text{H}_2\text{O}$  and pptd. with  $\text{NaCl}$  or  $\text{NH}_4\text{OH}$ ; in the first case is obtained phenonaphthothiazine chloride (Stahrross, C. A. 14, 1392), while  $\text{NH}_4\text{OH}$  gives the free base, unstable yellow flocks, giving on short warming with  $\text{Ac}_2\text{O}$  and a little  $\text{NaOAc}$  an *acetyl derivative*, stable dark red needles from  $\text{C}_6\text{H}_6$ , m.  $196^\circ$ , sol. in  $\text{C}_6\text{H}_6$  and alc. with orange-red, in concd.  $\text{H}_2\text{SO}_4$  with greenish blue-black color turning to a somewhat turbid violet on dild. with  $\text{H}_2\text{O}$ . Thiophenyl- $\beta$ -naphthylamine (C) was obtained in excellent yield (80%) by heating the components only 1 hr. at  $210^\circ$  at the highest and working up the product as before through the picrate. It seps. from ligroin in S-yellow needles, m.  $178^\circ$ , and shows a distinct green fluorescence in alc. and  $\text{C}_6\text{H}_6$ . *Acetyl derivative*, pptd. with  $\text{Ac}_2\text{O}$  and a little  $\text{ZnCl}_2$ , colorless crystals from  $\text{C}_6\text{H}_6$ , m.  $126^\circ$ . *Sulfoxide*, from C, suspended in considerable AcOH, treated in small portions with concd. aq.  $\text{NaNO}_2$  and pptd. with  $\text{H}_2\text{O}$  when the soln. has changed through orange-brown and brownish to almost colorless, granular crystals from  $\text{C}_6\text{H}_6\text{-EtOH}$ , decomp. about  $225^\circ$ , sol. in concd.  $\text{H}_2\text{SO}_4$  with blue-violet color; forming the azthionium salt; on addition of ice the soln. becomes a yellowish blood-red and with more  $\text{H}_2\text{O}$  slowly decolorizes and reprecipitates the *sulfoxide*. C in AcOH with concd. aq.  $\text{FeCl}_3$  dild. with AcOH gives, even with a large excess of  $\text{FeCl}_3$ , a dark green powdery cryst. ppt. of a *ferrie chloride double salt* of the quinhydrone



stage, containing about 12% Fe, sol. in  $H_2O$  with orange color but quickly decomp. and depositing dark flocks. If the oxidized soln., with the pptd. double salt in suspension, is treated with 20% aq.  $HClO_4$  and then with much  $H_2O$ , the Fe salt dissolves and is converted into the merquinoid  $\beta$ -naphthophenazthionium perchlorate, almost black microneedles. The holoquinoid perchlorate is best prepd. by dissolving 0.2 g. of the sulfoxide in just the necessary amt. of cold concd.  $H_2SO_4$  and treating the resulting violet-blue soln. of the diacid sulfate with 2 vols. of 20%  $HClO_4$ ; it seps. as a dark brown cryst. ppt. with brass luster, somewhat sol. in cold  $H_2O$  with orange color but quickly decomp. and becomes colorless. *Perbromide*, from C in AcOH and excess of Br in AcOH, dark brown-red cryst. powder, sol. in cold  $H_2O$  but quickly decomp. Thio- $\beta$ -dinaphthylamine (D) (*Ber.* 19, 2240(1886)) is obtained in 80% yield by heating 16 g.  $(\beta-C_{10}H_7)_2NH$  and 4 g. S at  $200-10^\circ$  at the highest for 10 min. only; it seps. from  $C_6H_6$  in light yellow needles, m.  $233^\circ$ , dissolves in  $C_6H_6$ , EtOH and AcOH with light yellow color and green fluorescence; *acetyl derivative*, long colorless needles from EtOH- $C_6H_6$ , m.  $208.5^\circ$ . *Sulfoxide*, long needles from EtOH- $C_6H_6$ , decomp. about  $212^\circ$ . Merquinoid *ferric chloride double salt*, fine graphite-black leaflets.  $\beta$ -Naphthazthionium perchlorate, heavy dark red cryst. powder.

CHAS. A. ROULLER

**Monograph on oxalic acid.** J. GROSSELD. *Z. ges. Kohlensäure Ind.* 26, 453-4 (1920); *Chimie & industrie* 5, 460(1921). A. P.-C.

**Iodometric estimation of mercaptans.** J. W. KIMBALL, R. L. KRAMER AND E. EMMET REID. *J. Am. Chem. Soc.* 43, 1199-1200(1921).—By taking advantage of the partition of HI between the disulfide and  $H_2O$ , Klason and Carlson's method for the estimation of mercaptans (*Ber.* 39, 738(1906)) has been so modified that the necessity for neutralizing the acid formed is eliminated. Into about 35 cc. N I in KI in a 250-cc. glass-stoppered bottle is introduced about 0.25 g. of the sample in a glass-stoppered weighing tube, the bottle shaken to release the sample and insure the free transfer of the I from the  $H_2O$  to the mercaptan layer and the excess of I titrated with 0.1 N  $Na_2S_2O_4$  and starch. The av. variations in 5-6 detns. each on Me, Et, Pr, Bu, sec-Bu, iso-Bu, iso-Am and Ph mercaptans were found to be 0.05-0.13%. C. A. R.

**$\beta$ ,  $\beta$ -Dichloroethyl sulfide.** DELÉPINE, FLEURY AND VILLE. *Compt. rend.* 172, 1238-40(1921).—The article is a summary of observations made on  $(ClCH_2CH_2)_2S$  (mustard gas) (A) during a wide experience gained from examn. of numerous samples of A and its components. 1. *Preparation*—A has been prepd. industrially by 3 methods, (a) from  $C_2H_4$  and  $S_2Cl_2$ , (b) from  $C_2H_4$  and  $S_2Cl_2$  to which sufficient Cl has been added to bring the compn. to  $SCl_2$  and (c) from  $S(CH_2CH_2OH)_2$  by esterification with HCl. 2. *Excess of sulfur in products*.—The products prepd. by (a) and (b) always contain an excess of S, either in soln. in some indeterminate form or, as has been suggested, combined as  $S:S(CH_2CH_2Cl)_2$ . (cf. Conant, Hartshorn and Richardson, *C. A.* 14, 1677). Pure A or that prepd. by method (c) is distinguished from the preceding products by the fact that it yields no  $H_2SO_4$  when oxidized with chromic-nitric mixt. whereas the others contain S oxidizable to  $H_2SO_4$  in quantities varying from 3 to 14%, depending upon whether  $SCl_2$  or  $S_2Cl_2$  has been used in their manif. 3. *Possible occurrence of isomers in the industrial products*.—A small quantity of HCl is always obtained by distn. *in vacuo* of the products made according to methods (a) and (b). Some of these may yield as much as 85% of a liquid f.  $10-13^\circ$  but never the pure A, which solidifies at  $14.10-14.15^\circ$ ; the distn. product is moreover always accompanied by portions which are still liquid at  $0^\circ$ . These liquid fractions, sepd. from 1 kg. of distillate and refractionated, yielded more of solid A. The new liquid fractions sepd. after cooling the distillates to  $-15^\circ$ , were once more fractionated, b<sub>10</sub>  $106-150^\circ$ . These last fractions had varying densities and solidified more or less at  $-10^\circ$  but surprisingly had practically the same S and Cl content as pure A;



they did differ from A, however, in the amt. of Cl hydrolyzable by H<sub>2</sub>O at 80°. The S oxidizable to H<sub>2</sub>SO<sub>4</sub> was practically nil. It is suggested that they probably consist of isomers such as ClCH<sub>2</sub>CH<sub>2</sub>SHClMe or S(CH<sub>2</sub>CHCl)<sub>2</sub>, ClCH<sub>2</sub>CH<sub>2</sub>SCH:CHCl, MeCHClSCH:CHCl, etc. formed, possibly, from higher chlorinated compds. by the splitting off of HCl, a view supported by the behavior of industrial products on rectification. The mol. wts. of these liquid fractions detd. in C<sub>6</sub>H<sub>6</sub> are of the order of that of A, actually 149-164. 4. Cryoscopic constant of  $\beta,\beta$ -dichloroethyl sulfide.—The f. p. const., K, of A was detd. to obtain some quant. idea of the impurities corresponding to the f. p. depressions noted in the crude distn. liquids. Raoult's law gave K = 60-2 but this value diminished very rapidly with moderate increases of the concn. Applying Louguine and DuPont's modified formula (cf. C. A. 7, 1316),  $dt = K_n/(n + N)$ , better agreement was realized and K = 38. The latter formula is valid up to  $dt = 10-15^\circ$ , using C<sub>6</sub>H<sub>6</sub>, PhCl, CCl<sub>4</sub> and CS<sub>2</sub>.

A. T. FRASCATI

Interaction of sulfur monochloride and organic acid amides. KUVERTI GOSAI NAIK. Imp. College Sci. Tech. J. Chem. Soc. 118, 1166-70(1921).—Oxamide, succinamide, malonamide, phthalanide and phthalimide do not react with S<sub>2</sub>Cl<sub>2</sub>. AcNH<sub>2</sub> gave N-sulfidobisacetamide, (AcNH)<sub>2</sub>S, slender needles, m. 192°. It decomps. AgNO<sub>3</sub> with the formation of Ag<sub>2</sub>S. On boiling with Na<sub>2</sub>CO<sub>3</sub> and then acidifying, H<sub>2</sub>S was evolved. N-Sulfidobisbenzamide, (PhCONH)<sub>2</sub>S, fibrous needles, m. 188°. This did not react with AgNO<sub>3</sub> nor with Na<sub>2</sub>CO<sub>3</sub>. N-Sulfidobisbutyramide, (C<sub>4</sub>H<sub>9</sub>CONH)<sub>2</sub>S, minute crystals, m. 175°. CO(NH<sub>2</sub>)<sub>2</sub> gave chiefly NH<sub>4</sub>Cl and S, with HCl. CS<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub> gave sulfidodithiocarbamide dihydrochloride [NH:C(NH<sub>2</sub>)S]<sub>2</sub>S<sub>2</sub>2HCl, pale yellow, m. 176-7°. Under H<sub>2</sub>O, it slowly decompd. With Na<sub>2</sub>CO<sub>3</sub>CO<sub>2</sub> was evolved. NaOH first pptd. S, and upon acidifying, H<sub>2</sub>S was evolved. CS(NHPh)<sub>2</sub> gave 3,6-dithio-1,2,4,5-tetraphenylhexahydro-1,2,4,5-tetrazine, CS(NPh.NPh)<sub>2</sub>CS, prisms, m. 160°; it is stable and is not affected by H<sub>2</sub>O. PhCONHPh gave trisulfidobisbenzimidide, (PhCONHC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>3</sub>, yellowish white, m. 244°. Disulfidobis-sulicylamide, [C<sub>6</sub>H<sub>4</sub>(OH)CONH]<sub>2</sub>S<sub>2</sub>, yellow, amorphous solid, decomp. 226°. C<sub>6</sub>H<sub>5</sub>(CO)<sub>2</sub>NK reacts with S<sub>2</sub>Cl<sub>2</sub> to form N-sulfidodiphtalimide, [C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N]<sub>2</sub>S, m. 190°, gradually decompd.

C. J. WHEAT

Organic arsenic compounds. II. Action of bromocyanogen on triethylarsine. WILHELM STEINKOPF AND JOHANNES MÜLLER. Techn. Hochschule Dresden. Ber. 54B, 841-7(1921); cf. C. A. 14, 3419.—AsEt<sub>3</sub>, b. 140°, is best prepd. (18 g. yield) from 93 g. EtBr and 21 g. Mg in 600 cc. Et<sub>2</sub>O slowly treated in ice-NaCl with 50 g. AsCl<sub>3</sub> in 120 cc. Et<sub>2</sub>O, decompd. with ice and HCl, dried with CaCl<sub>2</sub>, freed from Et<sub>2</sub>O below 38° in a CO<sub>2</sub> atm. and fractionated *in vacuo*; when a 1:10 soln. in Et<sub>2</sub>O is treated slowly in ice with a similar soln. of 1 mol. BrCN (distd. over CaCl<sub>2</sub>) it gives at once triethylarsine oxybromide, Et<sub>3</sub>As(OH)Br, needles from Me<sub>2</sub>CO, m. 149-50°, mol. wt. in freezing PhOH 251, very easily sol. in H<sub>2</sub>O with acid reaction. It is probably formed by hydrolysis from the intermediate triethylarsine bromocyanide, Et<sub>3</sub>As(CN)Br, which S. and M. succeeded in isolating by working in petr. ether in the app. described by Wolfram (C. A. 15, 2122); a prerequisite of success is that the app. and materials be absolutely dry, the petr. ether (b. 40-55°) was boiled several hrs. over Na-K alloy; the BrCN was distd. over CaCl<sub>2</sub> and then slowly over Na. The AsEt<sub>3</sub> in 10 parts petr. ether was treated slowly with 1 mol. BrCN in 20 parts petr. ether in an atm. of CO<sub>2</sub> dried with CaCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and P<sub>2</sub>O<sub>5</sub>. The product m. 67° immediately after its prepn. but on standing in the air goes over into the oxybromide; slowly heated under 12 mm. in a CO<sub>2</sub> atm. it decompd. at a bath temp. of about 110° into diethylarsine, b. 74°, m. -50°, has the typical odor of cacodyl compds. III. Action of bromocyanogen on cyclopentamethylenephenylarsine. WILHELM STEINKOPF AND ARTER WOLFRAM. Ibid. 848-57. — BrCN adds to cyclopentamethylphenylarsine (A) just as to AsEt<sub>3</sub> but at room temp.



there is no ring cleavage at all and even on distn. no detectable cleavage such as occurs with the analogous *N*-phenylpiperidine compd.; the As ring is therefore more stable than the piperidine ring towards BrCN. A (4.1 g.) in 10 vols. dry Et<sub>2</sub>O treated slowly at 17–30° with 1.9 g. BrCN (distd. over CaCl<sub>2</sub>) in 10 parts Et<sub>2</sub>O yields 5.3 g. *cyclopentamethylenephénylarsine oxybromide*, prisms from Me<sub>2</sub>CO or from EtOH-Et<sub>2</sub>O, m. 162.5°, mol. wt. in freezing PhOH 319.5, in CHBr<sub>3</sub> 601.9–5.5, forms a very strongly acid aq. soln., is also obtained by treating the dibromide in 96% alc. with Et<sub>2</sub>O. Working in the Wolfram app., with everything absolutely dry, it is possible to isolate the *bromocyanide*, an exceedingly light cryst. substance, m. 107° immediately after its prepn. A and BrCN also react vigorously when brought together without a solvent; if the mixt. is now warmed gently it evolves gases which burn with a distinct (CN)<sub>2</sub> flame and which, when passed through acidified AgNO<sub>3</sub> (to absorb any HCN) into Et<sub>2</sub>O yield considerable (CN)<sub>2</sub> to the latter. If the pure bromocyanide is cautiously warmed just to its m. p. no (CN)<sub>2</sub> is formed; the little HCN liberated (about 6% of the N) is probably due to traces of moisture. If dry CO<sub>2</sub> satd. with Br<sub>2</sub> is passed over the fused mass (0.14 g.), 0.12 g. Br is absorbed with formation of BrCN and a yellow oil which yields its As in ionized form to alkali, CH<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>Br)<sub>2</sub> remaining undissolved. If the fused bromocyanide is heated *in vacuo* up to 210° it yields considerable amts. of HCN and a little (CN)<sub>2</sub>. An app. is described in which the bromocyanide can be prepd., fused and fractionated *in vacuo* without exposure to the air; in this app., 15.3 g. fused bromocyanide (from 12.5 g. A and 6 g. BrCN) gave 9.9 g. yellow oil of unpleasant odor, b. 136–56°, which could not be completely sepd. into its components but in which reformed A could be shown to be present with certainty and the dibromide with great probability.

C. A. R.

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Action of aspirin on urethan (COMANDECC) 17. The synthesis of sugars from formaldehyde, carbon dioxide and water (EWART) 11D.

## 11—BIOLOGICAL CHEMISTRY

HATTIE L. JEFT, EDGAR G. MILLER, JR., AND WILLIAM J. GIES

### A—GENERAL

FRANK P. UNDERHILL

Application of the law of mass action to the results obtained in the reaction of  $\beta$ -galactosidase upon galactose in solutions of propyl alcohol and water. MARC BRIDEL. *Compt. rend.* 172, 1288–91 (1921).—In interpreting the results obtained by Bourquelot and Verdon on the action of emulsin upon glucose in soln. in MeOH and water, Bailly has arrived at the conclusion that "the law of mass action rules the diastasic reaction of synthesis and of hydrolysis of  $\beta$ -methylglucoside, and that the application of this law permits the prediction of the results of expts. effected in any concn. of water and MeOH." The formulas proposed by Bailly were applied to results obtained in the study of the action of emulsin upon galactose in soln. in mixts. of propyl alc. and water, with the object of detg. whether the law of mass action does actually hold for fermentation reactions, as might be thought from the fact that they are reversible. In the contrary case proof was acquired that equil. is not reached in the case of 45 and 55% propyl alcohols, because of the easy destruction of  $\beta$ -galactosidase at +30° in these alcohols, and of the excessively slow action of the enzyme at ordinary temps. In the weaker mixts., those less than 35% equil. is reached readily enough and the law holds, but for solns. stronger than 35% equil. was not reached during a period of 193 days. It would



be necessary in the case of these stronger solns. to prolong the reaction for months or even years to allow the ferment to reach equil., admitting that it could be reached. The difficulty of such expts. is readily conceivable. J. T. R. ANOREWS

**Demonstration of pyrrole compounds in protein.** N. TROENSEGAARD. *Z. physiol. Chem.* 112, 86-103(1921); *J. Chem. Soc.* 120, I, 201-2.—The author advances a theory that the protein mol. is composed mostly of heterocyclic compds., and attempts to prove it by demonstrating the presence of pyrrole substances in gliadin and gelatin. To avoid the decompn. of the pyrrole compds., the author did not use solvents which contained  $H_2O$ , and further, stabilized the pyrrole groups by introducing an acid radical. The gliadin was dissolved in MeOH-KOH which was free from  $H_2O$ . It was then neutralized, concd. in a vacuum, and acetylated with anhydrous AcON and  $Ac_2O$ . The acetylated product was dissolved in anhydrous AcOH and treated with glacial AcOH and HI on a water-bath. No melanin was formed. The pyrrole compds. were obtained by distn. with superheated steam. The dry gelatin was dissolved in anhydrous MeOH-KOH, neutralized with AcOH, treated with amyl alc., the MeOH removed by distn., and the paste residue treated with amyl alc. and Na, and then with  $CO_2$ , and after adding  $H_2O$  extd. with  $Et_2O$ . The latter and the amyl alc. were then distd. off, leaving the pyrrole substances behind. H. V. ATKINSON

**Protein chemistry. I. The capacity of combining with iodine and the constitution of the proteins.** F. BLUM AND E. STRAUSS. *Z. physiol. Chem.* 112, 111-150(1921); *J. Chem. Soc.* 120, I, 199.—From a study of the nature of the chem. combination of I with proteins, it is concluded that I entering into combination with proteins is not attached to the C ring only, but is also taken up by imino groups. The latter I is easily removed from the compd. by reduction with  $SO_2$ . The N-f was found to be in a constant relation to the C-I. In the action of I on proteins, substitution and oxidation take place, involving the loss of a biuret group and alteration in tryptophan and cystine complexes. In case of partial oxidation, the iodated proteins thus obtained contain C-I, but no N-I, and do not give the biuret reaction on degradation with these conditions. The introduction of the I into a mol. and the heating of the protein after the removal of the N-I, makes the protein resistant to peptic digestion. II. Iodoglobulin. EDWARD STRAUSS AND RUDOLF GRÜTZNER. *Z. physiol. Chem.* 112, 160-75; *J. Chem. Soc.* 120, I, 200.—The above method was applied to globin and the fully iodized protein was found to contain 11.4% I; after removal of the N-f it contained 7.6% I. Hence a mol. wt. of 3214 is deduced for globin. H. V. ATKINSON

**Secondary naphthol reaction.** W. LOELE. *Centr. allgem. Path.* 31, 440-52(1921), cf. *C. A.* 14, 2373, 2349.—Aldamine has the property of changing plant and animal nucleoli so that they give a black naphthol reaction. The tissues of the muscles of the swan possess a similar property when fixed in formalin. After several months, certainly after 7-8 months, the primary naphthol reaction of the mucous cells of the foot becomes weaker, the nucleoli of the epithelial cells turn black in naphthol soln. The cells of the ovary and intestinal tract give good naphthol reactions after 3 months. Plant tissues left in dil. naphthol soln. (1:10,000) for several days seldom show a positive secondary black reaction of the nuclear and protoplasmic granules. The black protoplasmic granules lie in spiral, light bands within the primary positive masses. E. B. FRICK

**Coagulation of the blood: A study of the anti-coagulant action of sodium citrate and of the part played by calcium in the blood.** MARCEL BLOCH. Paris. *Lancet* 1920, II, 301-4.—Na citrate when added to blood renders it incoagulable, but unlike oxalate and fluoride it does not act by pptg. Ca. It immobilizes the Ca salts of the blood and prevents the transformation of the prothrombin ferment into fibrin. Blood plasma is a colloidal soln. containing electrolytic precipitants, the most important of which are the Ca salts; Na citrate acts as a stabilizer of the colloidal blood soln. and prevents the



electrolytic Ca salts from exercising their peculiar pptg. properties, and this without in any way affecting the quantities of dissolved Ca salts.

E. B. FINK

**Experimental studies on diffusion through the cornea. Diffusion and iontophoresis of optochin and zinc sulfate.** M. GOLDSCHMIDT. *Arch. Ophthalm.* 103, 280-91 (1920); *Physiol. Abstracts* 6, 83-4.—The celerity of diffusion of Zn is doubled under the influence of the elec. current. The iontophoresis (cataphoresis) with optochin is 140 times more rapid than diffusion (investigations on the cornea of a bullock). H. G.

**Enzyme action. VII. Influence of additions (toluene, chloroform, thymol and neutral salts) on the fermentative decomposition of dipeptides by means of yeast extract.** E. ABDERHALDEN AND A. FODOR. *Fermentforschung* 4, 191-208(1921); *Physiol. Abstracts* 6, 96-7.—Addition of toluene,  $\text{CHCl}_3$ , and thymol causes no change of the activity of the enzyme, because these substances have no influence on the colloidal state. The influence of neutral salts depends on the colloidal state of the enzyme. Addition of 0.66 equiv. neutral salts per l. effects, first a little furtherance, but soon after an inhibition of the enzyme action. KI and KCNS inhibit, even in the above-mentioned concns., and KCl, KBr,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$  show, in somewhat higher concns., considerable inhibition. The degree of the optimal H-ion concn. is displaced, in the presence of neutral salts, to the acid side. **VIII. Production of enzyme sols from yeast phosphoproteins. The activity of the sols as a function of the colloidal state.** A. FODOR. *Ibid* 209-29; *Physiol. Abstracts* 6, 97.—Yeast phosphoproteins can be prepd. from yeast exts. by dil. acids; they yield sols of varying stability according to the H-ion content of the soln. These sols show fermentative actions on polypeptides. This effect is parallel to the degree of dispersity, as observed by the ultramicroscope. It decreases with increase of the acid used. By alkali alone or alk.-reacting Na phosphates, the degree of dispersity and of activity is higher; but above a certain concn. considerable hydration takes place, and the ultravisible particles disappear. Addition of neutral salts (KCl) causes activity in small quantities with higher concns. of acid. Inactive phosphoprotein (obtained by acids, alc.) of yeast can be again made active (with the reappearance of increased dispersity) by alkali, together with KCl.

H. G.

**The relation of the sedimentation velocity of the red blood corpuscles to the dialyzable compounds present in the blood plasma. Relation to the protective enzymes.** E. ABDERHALDEN. *Fermentforschung* 4, 230-41(1921); *Physiol. Abstracts* 6, 78.—Substances are present in the plasma of pregnant women which increase the rapidity of sedimentation of red cells. Blood corpuscles of normal persons settle quickly in the plasma of a pregnant person; the cells of pregnant women settle slowly in normal plasma. The substance (cleavage product?) passes through a dialyzer. Addition of "placenta peptone" to the blood of pregnancy has an accelerating influence, but not the addition of alanine or glycine.

H. G.

**The coenzyme (complement) of diastase.** W. BIEDERMANN. *Fermentforschung* 4, 258-300(1921); *Physiol. Abstracts* 6, 13-4.—Both animal and vegetable diastases consist of a thermostable (org.) component (zymogen or proenzyme) which is by itself inactive and of a thermostabile coenzyme or activators (the ions of numerous salts). Dialysis does not yield totally inactive solns., but the absorption of the org. component by glass is a method by which such inactive enzymes can be obtained. In the coenzymes anions have the chief effect, but the cations are not without influence. NaCl and KCNS have the greatest effect, then KCl, KBr, NaBr,  $\text{NH}_4\text{Cl}$ , the chlorides of Ca, Mg, Sr, Ba, the nitrates, iodides, and sulfates follow in order. Very small quantities of the salts can activate various quantities of the proenzyme. The optimum occurs at the neutral point. The smallest addition of free acid or alkali is sufficient to inhibit the effect and then to destroy the enzymes. Unsats. salts act in another way. Not only the primary alk. phosphates, but also acid Na citrate (0.3%), activate salt-free



diastase in spite of their reaction. Inhibition is the result of higher concns. The secondary phosphates and  $\text{NaHCO}_3$  activate in concns. which in acid salts cause inhibition (1%). H ions cause absolute inhibition sooner than the same increase of OH ions. But the inhibition is much greater under the influence of the diphosphates and the bicarbonate than in monophosphate solns. of the same concn. This relative inhibition of the diphosphate diastase can be suddenly removed by the smallest additions of NaCl (or similar neutral salt) without change of the reaction. Addition of NaCl to a neutral phosphate mixt. causes a diastatic activity which surpasses all other combinations with neutral salts. Mixed human saliva contains such a combination of inorg. salts, which has the best effect on the activity of the proenzyme. This combination of ions is the same, which effects the "autolysis" of amylose, as shown in B's earlier work.

H. G.

**Bilirubin content of human serum of the healthy and the sick.** R. BOTZIAN. *Mittell. Grenzgebiet. d. Med. u. Chirurg.* **32**, 549-66(1920); *Physiol. Abstracts* **6**, 39. —The bilirubin content shows fluctuations of short wave length in cases of hemolytic icterus. The "hemolytic" bilirubin gives no direct diazo reaction (in some cases the reaction is only retarded). The extirpation of the spleen causes the disappearance of the icterus and decreases the bilirubin content. But  $4\frac{1}{2}$  months after the operation the bilirubin content increases again, in consequence of compensatory growth of reticulo-endothelial tissue. At the same time, the hemolytic bilirubin is changed into "Stauungsbilirubin," which gives the direct and indirect diazo reaction. The same quantity of bile pigment is found in the arterial and venous blood of the spleen.

H. G.

**The influence of sodium fluoride on the activity of pancreatic diastase.** S. LANG AND H. LANG. *Biochem. Z.* **114**, 165-93(1921). —The production of glucose and maltose from oat and sol. starch by the action of freshly prepd. pancreatic diastase in the presence of various aunts. of NaF was detd. by polarization and titration of the residues. The protocols of the expts. are given in detail. The results show that NaF retards the diastatic decompn. of starch, the total amt. of end products decreased with increasing NaF concns., although at NaF concns. from 0.005% to 0.03% there does appear to be a slight accelerating effect. This is not a const. occurrence, however. The most rapid inhibition of total sugar formation occurs at a NaF concn. of 0.25%, the effect at higher concns. running an asymptotic course. The ratio of glucose to the total sugar rises with increasing NaF concn. and reaches a relatively max. value of 60-75% at 0.25 to 1.0% NaF. This increase of glucose formation from starch which occurs almost parallel with the decrease in maltose formation with increasing NaF concn. leads to the conclusion that the total activity of diastase consists in a certain mutual combination of amylase and maltase effect, a combination which, notwithstanding the undoubted specificity of the 2 enzymes results in facilitation of the one when the other is inhibited.

F. S. HAMMETT

**The action of metallic copper and silver on diastase. A contribution to the so-called oligodynamic phenomena.** A. LUGER. *Biochem. Z.* **117**, 153-60(1921). — Expts. are reported in which the action of taka-diastase 1:1000 on sol. starch in the presence of metallic Cu or Ag alone and in the presence of KCN, Na,  $\text{S}_2\text{O}_3$ ,  $\text{K}_2\text{S}$  and NaCl. was studied. The effect of  $\text{HgCl}_2$  under like conditions was observed. When the diastatic action has been retarded by the metals it can be reactivated by the addition of these compds. This leads to the conclusion that the so-called oligodynamic action of metals is due only to their soln. in the various media used.

F. S. HAMMETT

**Supplementary to the work of E. Herzfeld and R. Klinger "Are there protective enzymes against polysaccharides?"** EMIL ANDERHALDEN. *Biochem. Z.* **117**, 161-5 (1921). —A. raises the claim that Herzfeld and Klinger (*C. A.* **15**, 1909) have failed to contribute any new data in their report, and that he has repeatedly stated that it



is not possible to produce in the blood with regularity and certainty an enzyme which splits cane sugar, when this compd. has been parenterally administered.

F. S. HAMMETT

**Chemical composition of the brain.** TOMIIDE SHIMIZU. *Biochem. Z.* 117, 252-62(1921).—By methods which are described in some detail and which because of their multiplicity cannot be abstracted S. obtained the following amts. of substances from 35 kg. of ox brain. Glycocoll, none; alanine, 0.24 g.; valine, 0.13 g.; leucine, 0.09 g.; isoleucine, 0.09 g.; proline 0.25 g.; phenylalanine, 0.03 g.; glutamic acid, 0.10 g.; aspartic acid, present; tyrosine, 0.18 g.; histidine, 0.19 g.; arginine, 0.21 g.; lysine, 0.70 g.; adenine, 2.42 g.; guanine, 0.42 g.; xanthine 1.33 g.; hypoxanthine, 0.18 g.; creatinine, 0.22 g.; cytosine, 0.03 g.; thymine-uracil, 1.26 g.; choline, 0.57 g.; and serine, 0.47 g. Demonstrable amts. of *D*-lactic acid, succinic acid and inositol were found.

F. S. HAMMETT

**The significance of acidity in the hydroxynitrile synthesis and the non-existence of Rosenthaler's syn-emulsin.** E. NORDEFELDT. *Biochem. Z.* 118, 15-33(1921).—This paper is a report of a study of the role of emulsin in the reaction  $C_6H_5CHO + HCN \rightleftharpoons C_6H_5CH(CN)OH$  (cf. *C. A.* 7, 2583; 8, 1792, 1796). An extensive résumé of the literature is given. There were used for the investigation solns. of benzaldehyde in 47% EtOH; alc. solns. of HCN and emulsin prepd. from bitter almonds ground finely and added to the reaction mixts. All detns. were made at a temp. of 17-18°. The reaction mixts. were buffered to different  $p_H$  by acetate mixts. or made acid or alk. with  $H_2SO_4$  and NaOH so that a  $p_H$  range from 2.0 to 8.0 was obtained. The results of the reactions were detd. by au estn. of the residual HCN. It is shown that a decreasing acidity favors the synthesis. The results speak against the idea of Rosenthaler that emulsin exerts an enzyme activity in the hydroxynitrile equilibrium reaction. The increase in the velocity of the synthetic reaction is attributed to the probability that the emulsin prepn. combines with more or less of the free  $C_6H_5COOH$  of the reaction mixt. whereby the  $p_H$  and the reaction velocity are increased. The increase in the amt. of hydroxynitrile in the presence of emulsin is explained on the grounds that equil. is reached more rapidly in a mixt. where the  $C_6H_5COOH$  is bound by the emulsin, than in a mixt. where the acid present retards the process. Syn-emulsin, which is obtained when emulsin is first treated with acid and then made neutral with alkali, activates the synthesis because the neutral point  $p_H = 7$  has been developed and the acidity is then so unnoticeable that the synthesis proceeds with extraordinary rapidity. The action of this prepn. is not enzymatic. Rosenthaler's "diaemulsin," which results from treating emulsin with  $CuSO_4$  or  $MgSO_4$ , is also not an enzyme on the same line of reasoning. The only specific effect which emulsin exerts on a mixt. of benzaldehyde and HCN is the production of asymmetric hydroxynitrile.

F. S. HAMMETT

**The enzyme phosphatase-phosphatase.** H. P. BARENDRECHT. *Biochem. Z.* 118, 254-5(1921).—B. discusses the observation of Euler and co-workers (*Biochem. Z.* 37, 314) that phosphatase, the alleged enzyme which brings about synthesis of hexose-phosphates, instead of losing its activity on heating at 40°, shows an increased ability to bring about the synthesis. He disapproves the idea that this is sufficient evidence for the existence of a synthesizing enzyme "phosphatase" separate from the hydrolytic enzyme "phosphatase" which splits the hexose-phosphates and cites his own studies on urease as examples of the possible reversibility of enzyme action. (Cf. *C. A.* 14, 748).

F. S. HAMMETT

**The action of metals on toxins.** F. ERDSTEIN AND L. FÜRTH. *Biochem. Z.* 118, 256-8(1921).—Dry tetanus toxin was dissolved in physiol. NaCl soln. in 0.01 to 100 concn. and the mixt. divided into 2 parts. To one was added a spiral of metallic Cu. After an interval, the action of the Cu-treated and of the untreated toxin soln. was



tested on mice with the result that the mixt. to which the Cu had been added was non-toxic up to 8 times the dose of the untreated toxin soln., which produced death. When similar expts. were carried out, metallic Ag being used instead of the Cu, only a slight diminution of toxicity was found to take place even after 4 to 8 day contact. A complete detoxication of the tetanus toxin could not be produced by Ag. Further expts. showed that diastase activity is retarded by a  $1:10^{11}$   $\text{CuSO}_4$  soln. and by a  $1:10^4$  soln. of tetanus toxin in which a Cu spiral had been allowed to stay for 24 hrs. on ice. It is evident from this that in 24 hrs. there goes into soln. in 50 cc. of tetanus toxin soln. as much Cu from the metallic spiral as corresponds to an equimol. soln. of  $\text{CuSO}_4$   $1:10^4$  diln. The results of repeated injections into mice of a tetanus toxin soln. in contact with metallic Cu lead to the conclusion that the process of detoxication involves the destruction of the entire toxin mol. and not of any particular component. No reactivation of the toxin could be produced.

F. S. H.

**The influence of light on the blood.** E. ASCHENHEIM AND S. MEYER. *Z. exper. Path. Therap.* 22, 22-33(1921).—On the basis of 220 examins. of blood specimens from 16 children the conclusion is reached that light affects the absolute and relative numbers of the formed elements of the blood. No marked differences that were valid could be found between the action of natural and artificial light. The reaction of the blood to illumination is the production of an increased number of non-granulated mononuclear leucocytes, apparently at the expense of the polymorphic neutrophils. The eosinophils and mast cells are not disturbed. The hemoglobin and erythrocyte content is increased. The intensity of the reaction is dependent on the length of the period of illumination. Young children react in a shorter time and give a greater increase in the immature cells than do older children.

F. S. HAMMETT

**Note on the permeability of the red corpuscles for amino acids.** SHUZO KOZAWA AND NOBU MIYAMOTO. *Biochem. J.* 15, 167-70(1921).—Red corpuscles of ox, man and goat are, to a certain extent, permeable for amino acids, such as glycocoll and histidine.

B. HARROW

**Chemical investigation of amylases and related enzymes.** H. C. SHERMAN. Columbia Univ. *Carnegie Inst. Washington Yearbook* 18, 328-30(1919).—A neutral soln. of Na aspartate corrected the abnormally low results obtained by the action of purified pancreatic amylase upon potato starch which had previously been purified by washing with very dil. alkali and subsequent thorough washing with especially purified water. The neutral soln. of Na aspartate also accelerated the rate of hydrolysis of wheat, maize, rice, and potato starches by purified pancreatic amylase, by purified malt amylase, by com. pancreatin, or by saliva, but had no such action on their hydrolysis by a simple ext. of malt, or by either the com. or a lab. prepn. of the amylase of *Aspergillus oryzae*. When sol. starch was used as the substrate and the reducing sugar produced was detd. gravimetrically, similar results were obtained. When this technique was used, and asparagine was substituted for Na aspartate, essentially similar results were obtained; however, the asparagine apparently produced a slight increase in the activity of taka-diastase. When both asparagine and a neutral soln. of Na aspartate were added to a digestion mixt., the results were such as were obtained by use of either of the 2 compds. in its optimum concn. Thus the activating effects of aspartic acid and asparagine were interchangeable rather than additive; their effect was not due to a change in the H-ion concn., nor to the Na ion, nor to the mere concn. of electrolyte, since optimum concns. of chlorides and phosphates were already present. The effect was, in a sense, specific, since neutral Na aspartate increased the enzymic activity when the optimum amts. of chlorides and phosphates were present, but could not completely replace chlorides in the activation of pancreatic amylase. JOSEPH S. HENRIKSEN

**Formation of enzymes.** H. STAUB. Univ. Basel. *Helvetica Chim. Acta* 4,



281-7(1921).—The ability of the body to assimilate 20 g. of glucose, taken by mouth, may be measured by the duration and degree of the resulting hyperglucemia. The ability is good if carbohydrates have been ingested previously within a reasonable time, and is decreased after deprivation of carbohydrates. On a diet containing carbohydrates, the assimilation enzymes, which govern intermediary carbohydrate metabolism, are present in the organism in sufficient quantities to prevent an excessively high alimentary hyperglucemia and to facilitate rapid assimilation. After deprivation of carbohydrates, a scarcity of these enzymes exists, and, therefore, an imperfect power of assimilation. Hence, in the normal metabolism of carbohydrates, it is a question of the secretion of enzymes to meet conditions. After ingestion of carbohydrates, enzymes are secreted in excess for assimilation of the food and are present in the body 10 to 15 hrs. later in so abundant an amt. that ingested glucose is promptly assimilated. On deprivation of carbohydrates for a longer period than this, a shortage of carbohydrate-assimilating enzymes gradually occurs since no demand for them exists. If glucose is then ingested, at first it is assimilated with difficulty or not at all, and the alimentary hyperglucemia attains a high value. However, the ingested glucose then acts again as a stimulus for the secretion of the enzymes; and, as soon as this secretion has begun—it occurs quickly—a decrease in the % of blood sugar and a return of the latter to its normal level take place. A specific formation of these enzymes occurs in man if carbohydrates be ingested in physiological amts. These enzymes may be designated equilibrium enzymes since they restore the equil. which has been destroyed by too high a concn. of an ingested substance in the blood.

JOSEPH S. HEPBURN

**Photochemistry of the sensitivity of animals to light.** SELIG HECHT. Creighton Univ. *J. Optical Soc. America* 5, 227-31(1921).—The expld. animals were a clam (*Mya arenaria*) and an ascidian. The action of light is probably photochem., since the product of the intensity of illumination by the sensitization period or time of necessary exposure is equal to a const., and since the temp. coeff. for the action of light on the sensory activity of the animals is approx. 1 for an increase of  $10^{\circ}$  in temp., showing that a definite quantity of photochem. transformation is required to produce a stimulating effect regardless of the temp. The animals show a well marked adaptation to light, failing to give more than a single response even to intense sunlight. They have an equally prominent adaptation to the dark. During adaptation to light, the latter decomposes a sensitive substance, and also produces a decrease in sensitivity. During adaptation to the darkness return of sensitivity occurs, possibly as a result of the formation of fresh sensitive material. Light breaks up a sensitive substance into its precursors and these precursors reunite in the dark to regenerate the sensitive substance. The adaptation to the dark follows the course of a bimolecular reaction, two precursors (or a precursor and an accessory),  $P$  and  $A$ , combining to form the sensitive substance,  $S$ ; the temp. coeff. of this adaptation to the dark is 2.4 for an increase of  $10^{\circ}$  in temp. The reaction time in adaptation to the light is subdivided into the sensitization period, during which illumination is actually necessary, and the latent period during which the animals may be in the dark and yet give their response at the end just as though they had been illuminated all the time. During this latent period, an inert substance  $L$  is converted into a chem. active substance  $T$  which then acts on the nerve to produce the outgoing sensory stimulus; this reaction, converting  $L$  into  $T$ , is catalyzed by the freshly formed photochem. decompn. products  $P$  and  $A$ . The process of dark adaptation in the human eye is fundamentally similar in principle to the process occurring in these lower animals. Cf. *C. A.* 15, 1044.

JOSEPH S. HEPBURN

**Interaction between albuminous substances and saline solutions.** ALMROTH E. WRIGHT. *Proc. Roy. Soc. (London)* 92B, 118-24(1921).—If serum be superposed on a hypertonic NaCl soln., best a 5% to 8% NaCl soln., the 2 liquids mix. by pseudo-



podial interpenetration. A similar effect is obtained if the NaCl soln. be replaced by a soln. of a salt such as  $\text{Na}_2\text{SO}_4$ , KCl,  $\text{K}_2\text{SO}_4$ , and  $\text{MgSO}_4$ , or of sucrose. Very concd. solns. give less striking results. The same phenomenon occurs, though less rapidly, if a hypotonic NaCl soln. be superposed on serum, but does not take place when water is superposed on serum. When hypertonic NaCl soln. is superposed on infected serum, the microorganisms are carried into the saline soln. The hypertonic NaCl soln. is an agent "capable of drawing out from the cavities and cul-de-sacs of a wound and porous tissues, along with the serum lodged there, the microbes which may be suspended in it." The saline soln. is also carried into the cavities, cul-de-sacs, and porous tissues, and may possibly be made a vehicle for the transport of bactericides into these places; however the bactericidal power may be lost by reaction with the proteins of the body. Diffusion is considered to be an interfusion of two liquids. "If it be permissible to generalize from the case of what happens when albuminous substances and saline solns. are brought into conjunction, it may be suggested that it would be appropriate explicitly to recognize the existence of *tractor* or *drawing forces*, and more generally of *interaction* as an agency which may coöperate with diffusion and assist in bringing about interfusion."

JOSEPH S. HEPBURN

The sedimentation velocity of erythrocytes. I. Human blood. GEORG LINZENMEIER. *Arch. ges. Physiol.* **181**, 109-83 (1920). Freshly drawn blood from normal and pregnant women was tested, after centrifugation and washing of the red cells, for sedimentation velocity when the cells were recombined with their homologous plasma in the ratio of 1 : 3 or 2 : 3. Other portions of the same plasma were shaken with various adsorbing agents. These adsorbed plasma were then used with red cells in similar detns. Comparative measurements upon normal blood and on that taken during pregnancy showed that (before shaking) the sedimentation velocity of the normal blood was decidedly less, 12 mm. in 10 min. as compared with 13 mm. in 10 min. for the blood taken during pregnancy. With both types of blood shaking the plasma with adsorbents for positively charged particles, such as animal charcoal, kaolin, bolus alba, and to a much less degree with talcum, very markedly reduced the velocity of sedimentation. Agents, such as the oxides of Fe and Ce or the hydroxides of Fe and Al, which adsorb negatively charged particles, either do not alter the velocity of sedimentation at all or in some instances accelerate it. Inactivation of the plasma brought about by heating at 56 degrees causes a retardation of sedimentation, the change in velocity being roughly proportional to the duration of heating. In plasma heated at 56 degrees for 3 hrs. the sedimentation velocity is only 50% of that in plasma heated for 20 min. Naturally, the temp. at which the sedimentation reaction is carried out is important; low temps. retard the reaction. The effect of defibrination was marked. A sedimentation of 12 mm. occurred in 50 min. with citrated blood, in 30 min. with humified blood, and in 70-1 min. with defibrinated blood. This suggests that the fibrinogen is a regulating factor in the reaction. Additional evidence of the relationship of fibrinogen to the process is adduced from the fact that maternal blood sedimented 18 mm. in 50 min., while that from the child, taken from the umbilical cord, required 1185 min. to settle the same distance. The addition of narcotics, anhydrous, phenylurea, isobutylmethane, acetophenone, heptyl alcohol to the plasma-cell mixtures delayed sedimentation; while gelatin, gum arabic, mucin, i.e., starch paste, and the contents of ovarian cysts, increased the velocity. The difference in sedimentation velocity between normal blood and that taken from pregnant women is interpreted as meaning that during pregnancy some substance appears in the plasma which possesses an adsorptive capacity and which alters the charge of the corpuscles.

G. H. S.

The application of the theory of Brownian motion to the irregular motility of lower forms of life. REINHOLD FÖRTH. *Arch. ges. Physiol.* **184**, 204-19 (1920). Part III.



suspended in water, or in water contg. tragacanth, were placed in a hemocytometer and their motility was observed microscopically and recorded. The results are subjected to mathematical treatment and the values for various consts. are established. G. H. S.

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

A simple method for the preparation of creatinine from meat extract. H. STEUDEL. Univ. Berlin. *Z. physiol. Chem.* 112, 53-4(1921).—Liebig's meat ext. is treated with 4 times its wt. of hot abs. alc. in 2 successive portions and the clear supernatant soln. distd. until a sirupy liquid is formed, from which creatinine crystallizes. These crystals are recrystd. from  $H_2O$  without animal charcoal. One kg. meat ext. yields 30 g. air-dried creatinine.

H. V. ATKINSON

Blood sugar determination. H. SCHIROKAUER. *Berlin. klin. Woch.* 57, 227-9 (1920); *Physiol. Abstracts* 5, 558.—Using methods recently introduced (methods named and briefly described), S. finds that in diabetes the sugar bound to corpuscles varies greatly, but the percentages in whole blood are less than those in the plasma. H. G.

Physiopathological study of adrenaline. H. SEPÚLVEDA. *Inaug. Dissertation*, Santiago, 1917; *Physiol. Abstracts* 6, 71.—To est. adrenaline in the blood, S. adds the blood serum drop by drop to 4 or 5 cc. of a 5% soln. of  $Hg(NO_3)_2$  in 0.1 N  $AgNO_3$  until there is complete pptn. The ppt. is filtered off, and to the filtrate is added drop by drop standardized  $KMnO_4$  soln. until a light rose coloration is produced. Normally the adrenaline reaches a max. value of 0.30 g. per mil. The detns. in pathol. conditions appear to have considerable prognostic value.

H. G.

Preparation of peptone. M. B. SOPARKAR. *Rept. Bombay Bact. Lab.* 1918, pp. 9, 10; *Expt. Sta. Record* 43, 502.—A satisfactory substitute for Witte's peptone has been prepd. as follows: Casein obtained from skim milk is digested for a few days at 40° with proteolytic enzymes derived from the pancreatic glands of goats. Further digestion is then prevented by boiling, and the resulting ext., consisting of a mixt. of proteoses, peptones, polypeptides, and amino acids, is evapd. to dryness and pulverized.

H. G.

The separation of  $\beta$ -aminoethyl alcohol from choline. E. FOURNEAU AND A. GONZALES. *Anales soc. espan. fis. quim.* 19, 151-5(1921).—The mixed hydrochlorides of the two bases are obtained by the acid hydrolysis of a lecithin and cephalin mixt. obtained from eggs. The dry hydrochlorides are dissolved in MeOH and the soln. is treated with the theoretical quantity of MeONa necessary to liberate the bases. The NaCl formed is filtered off and the soln. evapd. to dryness *in vacuo*. The residue is dissolved in abs. ether and an ethereal soln. of one-half mol. of the chloride of naphthalene-sulfonic acid is added. A reaction takes place with evolution of heat. At the end of one-half hour is added one-half mol. of NaOH in normal aq. soln. The mixt. is shaken, the aq. layer sep'd., washed with ether, and acidified with dil. HCl to ppt. the  $\beta$ -naphthalene-sulfuryl- $\beta$ -aminoethyl alcohol formed. Sometimes the ppt. seps. in the form of an oil which solidifies after standing for some time. The ppt., after recrystn. from toluene, melts at 86°. Yield, about 75% of the theoretical.

L. E. GILSON

The preservation of blood with allyl alcohol. E. SALKOWSKI. *Biochem. Z.* 118, 244-57(1921).—S. considers that allyl alcohol is the ideal blood preservative on account of its relative cheapness, its miscibility with  $H_2O$ , its preserving ability, and because it causes no changes in the blood and can be completely removed when the blood is dried to a powder. It is effective in preventing putrefaction for 5 or 6 days when present in a concn. of 0.5 to 0.6%.

F. S. HAMMETT

Quantitative determination of the duration of caffeine excretion in man by a new biological method. EDWARD FRIEDBERG. *Biochem. Z.* 118, 164-84(1921).—Urine



from which the caffeine is to be extd. is first made slightly alk. with a few drops of a 5% soln. of  $\text{Na}_2\text{CO}_3$ . It is then evapd. on a water bath with the addition of dry  $\text{CaSO}_4$ . The residue is finally dried in a vacuum over  $\text{H}_2\text{SO}_4$ . The finely powdered mixt. is extd. with 20 cc. petroleum ether (50-80°) in a reflux condenser. The solvent is removed by suction and the residue is extd. for an hr. with 20 cc.  $\text{H}_2\text{O}$ -free  $\text{CHCl}_3$ . This exts. the caffeine. The  $\text{CHCl}_3$  soln. of caffeine is dried with 1 g. anhydrous  $\text{Na}_2\text{SO}_4$ , cooled, filtered, and the  $\text{CHCl}_3$  distd. off. The residue is dissolved in 0.25 to 2 cc. Ringer soln. and its caffeine content tested on muscle fibers from the sartorius of the frog. The test is carried out under the microscope; it consists in adding 0.1 cc. of the soln. to be tested to a fiber in a drop of Ringer soln., noting the degree of contraction and then dilg. the ext. until the threshold of the reaction is reached. The amt. of ext. obtained from the urine multiplied by the diln., divided by 3500 gives the amt. of caffeine excreted. F. claims to be able to det. 0.00007 g. caffeine by this method. The error of detn. is around 10%. Acknowledgment is made that methylxanthine may be present and give the reaction. By this method it was found that the amt. of caffeine excreted in single lots of urine is partly dependent on the amt. of urine. Diuresis induces increased caffeine excretion. However, the relation is not exact, for when a dry diet plus caffeine is given there is a high caffeine content of the urine, which diminishes when diuresis sets in. The diuretic action of caffeine is only partly dependent on the size of the ingested dose or its apparent concn. in the blood. The  $\text{H}_2\text{O}$  content of the organism plays a significant role for in hydremia very small doses produce excessive diuresis. Ten mg. is the smallest amt. of pure caffeine which when given by mouth yields a positive test in the urine. The ingestion of relatively small amts. of coffee yield positive caffeine tests in the urine. When caffeine sodium benzoate is injected subcutaneously methylxanthine appears in the urine after a time. The absorption by this method seems to be slower than when the compd. is given by mouth. When caffeine-containing tobacco is smoked, the drug is absorbed and the amts. excreted speak for a rapid and rather complete absorption of the caffeine in the smoke. Since the excretion of ingested caffeine falls off rather rapidly and is not quant. the conclusion is drawn that there takes place a rather rapid destruction of the drug in the human organism, a transformation to methylxanthine. A caffeine tolerance in the sense of an increased caffeine destruction on continued ingestion does not occur.

F. S. HAMMETT

**The quantitative determination of oxalic acid in urine** F. SALKOWSKI. *Biochem. Z.* **118**, 239-69 (1921).—A discussion of the work of Bau (C. A. **15**, 1546) on the problem. S. considers that filtration of the urine prior to analysis may yield low results because of loss of Ca oxalate in the sediment. Anhydrous  $\text{CaCl}_2$  is used to make up the 10% soln. of this salt. Ca oxalate may appear in urine as simulating bacterial forms. This type is an abortive form of the crystals in the form of quadratic prisms with pyramidal end pieces. The increase in oxalic acid which occasionally occurs when urine is allowed to stand for some time under sterile conditions is attributed to a production of this compd. through oxidation of uric acid or allantoin.

F. S. HAMMETT

**New and simple tests for alkali carbonates in the urine.** C. MITCHELL. *Med. Rec.* **99**, 516 (1921).—M. discards all previous tests for the alkali carbonates of urine and substitutes several of his own devising. The 1st consists in overlaying 2 to 3 cc. of urine in a small test-tube with 5 drops of a clear 1% soln. of  $\text{HgNO}_3$  in  $\text{H}_2\text{O}$ , the appearance of a dark ppt. in the upper stratum indicates amts. of carbonates of clinical significance. It is admitted that the Hg soln. ppts. sol. sulfides, which are shown to be the cause of the dark ppt. if this is not affected by the addition of 10 drops of 5%  $\text{NaOH}$ . If the ppt., however, is turned brown or gray and settles, carbonates and not sulfides are present. Drugs may interfere with the reaction. M. detts. the presence of  $(\text{NH}_4)_2\text{CO}_3$  by adding 2 to 5 drops of urine to 1 to 3 cc. of Nessler's reagent in a test-tube and noting



the appearance of a red floating ppt. If no  $(\text{NH}_4)_2\text{CO}_3$  is present a yellow ppt. is formed. Urines containing  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  are negative to the test but give a positive Hg test.

F. S. HAMMETT

**Estimation of blood sugar.** ERIC PONDER AND LAURANCE HOWIE, Univ. of Edinburgh. *Biochem. J.* 15, 171-74(1921).—A modification of the method of Folin and Wu (*C. A.* 14, 2353); the amount of blood required is readily obtained from the finger.

B. HARROW

**The silver reduction method for the demonstration of connective tissue fibers.** J. R. PERDRAU. *J. Path. Bact.* 24, 117(1921).—Thin sections are treated with 0.25%  $\text{KMnO}_4$  five minutes or longer, washed with water, and placed in Pal's decolorizer until white. They are then washed overnight in distd. water, and stained by Da Farro's modification of Beilschowsky's method (cf. *J. Physiol.* 52, 57-8(1919); 53, 92-6(1920)).

JOHN T. MYERS

**The estimation of the actual blood sugar in the healthy and in the sick.** WILHELM STREPP. *Arch. exp. Path. Pharm.* 90, 105-28(1921).—Methods of detg. blood sugar were compared in cases of diabetes, nephritis, and individuals with a normal metabolism. In the detn. of blood sugar by reduction a very important factor is the method of protein removal as well as the method of reduction. A considerable error may be introduced since many nitrogenous compds., uric acid, creatine, creatinine, amino acids, etc., possess reducing properties. For removal of such substances phosphotungstic acid is unquestionably superior to colloidal iron. Reduction methods give values for blood sugar which are usually 20-40% too high, and in some instances as much as 100% too high. Correct values can be obtained only when the polarization value corresponds with the fermentation value.

G. H. S.

**Methods of vital staining.** EDMUND NIRENSTEIN. *Arch. ges. Physiol.* 179, 233-337 (1920).—Vital staining may consist of a diffuse staining, a granule staining, or a staining brought about through phagocytic inclusion. The first two methods are those chiefly considered and a discussion of the mechanism of staining by these methods is presented. With paramecia, normal and abnormal forms, 120 different dyes were tested. The conclusion is reached that the processes of diffuse staining and granule staining are of essentially the same nature, the end results being simply quant. variations. A mixt. of oleic acid, almond oil, and diamylamine reacted with the dye solns. in water in a manner analogous to protoplasm. From studies upon this, and other findings, the author advances a modified lipid theory as the explanation of vital staining of the diffuse and granular types. Vital stains are only those substances which stain the plasma itself.

G. H. S.

**Detection and determination of veronal.** L. VAN ITALLIE AND (MISS) A. J. STEENHAUER. *Pharm. Weekblad* 58, 864-5(1921).—In the estn. of veronal in cases of suspected poisoning, it is best to use  $\text{EtOAc}$  for extg. veronal from the urine, feces, etc. No charcoal should be used, since it may adsorb up to 45% of the veronal from solu. After extn. the substance is best purified by treatment with  $\text{KMnO}_4$  in acid solu. It is possible to recover 100% of added veronal from urine, and 97% from vital organs.

JULIAN F. SMITH

Viscosimeter with temperature regulation (Hess) 1. Detection of acetone (PITARELLI) 7.

## C—BACTERIOLOGY

A. K. BALLS

**Effects of acids and the formation of soluble starches by mold fungi.** F. BOAS. *Botan. Centr. Beihefte* 36, Aht. 1, No. 1, 135-85(1919); *Expt. Sta. Record* 43, 523; cf. *C. A.* 14, 1129.—This is a detailed account of work which B. carried out during the years 1913-1917 with *Aspergillus niger*.

H. G.



**Contribution to the growth of the glanders bacillus with special reference to mallein formation.** H. VEHSE. *Monatsh. Prakt. Tierheilk.* 31, No. 7-8, 363-82(1920); *Expt. Sta. Record* 44, 478.—This article reports a study of the relative values of the protein-free and of bouillon media for the growth of glanders bacilli for the mallein test, and of the effect of different factors upon the growth of the bacillus. A protein-free nutritive medium consisting of 15 parts of  $\text{NaH}_2\text{PO}_4$ , 20 of  $\text{KH}_2\text{PO}_4$ , 3 of  $\text{MgSO}_4$ , 12.5 of Mg citrate, 25 of asparagine, and 100 of glycerol made up to 5,000 parts with distilled water was found to be as satisfactory as one contg. bouillon. The growth of the organism took place best in neutral or slightly acid media in the presence of between 4 and 5% of glycerol. Sucrose hindered and lactose favored the growth of the organism. Of the colored media litmus lactose agar gave good results, while neutral red agar afforded only scanty growth. H. G.

**Sulfur bacteria.** M. DÜGGELE. *Neujahrsbl. Naturf. Gesell. Zürich* 1920, No. 121, pp. 43; *Expt. Sta. Record* 44, 133.—This deals with the production and accumulation in nature of  $\text{H}_2\text{S}$  and the relation thereto of the so-called S bacteria. A section deals with denitrifying bacteria. The work concludes with a list of 166 titles bearing on the subject. H. G.

**Comparative studies of the ferment-retarding action of some chlorine derivatives of methane, ethane and ethylene.** H. PLAGGE. *Biochem. Z.* 118, 129-43(1921).—Yeast in active fermentation was the substrate used in these studies and the disappearance of added sugar and the  $\text{CO}_2$  evolution were detd. as measures of the effect of the various compds. on the activity of the yeast. Alcohol was added at times as solvent for the compds. used and its effect was detd. in appropriate controls. The influence of  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $(\text{CH}_3\text{Cl})_2$ ,  $\text{C}_2\text{H}_5\text{CHCl}_2$ ,  $\text{C}_2\text{H}_5\text{CH}_2\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{CHCl}_2$ ,  $\text{C}_2\text{H}_5\text{CH}_2\text{Cl}$ , and  $\text{C}_2\text{H}_5\text{CH}_2\text{Cl}$  was studied.  $\text{CH}_3\text{CHCl}_2$ ,  $(\text{CH}_3\text{Cl})_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CHCl}_2\text{CHCl}_2$  are toxic towards yeast-cell activity. The degree of their effect is dependent not on the concn. of the soln. but on the relation of the amt. of toxic compd. to the amt. of yeast present. F. S. HAMMETT

**Effect of acetaldehyde and methylene blue on the fermentation of glucose and fructose by yeast juice and zym in presence of phosphate and arsenate.** ARTHUR HARDEN AND F. R. HENLEY. *Biochem. Dept., Lister Inst. Biochem. J.* 15, 173-85 (1921).—In the fermentation of glucose in the presence of phosphate by zym or yeast-juice, acetaldehyde or methylene blue produces a remarkable acceleration in the early stages of the reaction. It is possible that these substances act as hydrogen acceptors (*C. A.* 15, 289). Acetaldehyde diminishes the time required by a mixt. of fructose and phosphate to attain its maximum rate of fermentation in presence of yeast juice or zym, but does not increase the max. rate obtainable. Acetaldehyde is about 50 times as effective as fructose (when molecular quantities are compared) in "inducing" fermentation in a mixt. of glucose with excess of phosphate. Arsenate does not affect the accelerating action of acetaldehyde in presence of phosphate in the fermentation of glucose and fructose by yeast juice, but considerably increases the rate attained with glucose, and to a less extent with fructose, when zym is used. Methylene blue produces an effect similar to that of acetaldehyde in the fermentation of both fructose and glucose by zym and yeast juice (in presence of phosphate.) BENJAMIN HARROW

**Lactic acid bacteria.** S. O. JENSEN. *Kgl. Danske Videnskab. Selskab. Skr. Naturvidensk. og Math. Afd. [8]* 5, 81-196(1919); *Expt. Sta. Rec.* 43, 680-1(1920).—The group of lactic acid bacteria includes both sphere-forms and rod-forms; these organisms do not contain catalase. They cannot decompose uncombined amino acids, and comparatively few have a marked proteolytic action. The cocci, which digest casein, act gradually, producing peptones, then amino acids. The rod-like forms, which attack casein, cleave amino acids from the mol. of that protein without intermediate



formation of peptone. These organisms apparently produce from peptone a group of polypeptides which are not pptd. by phosphotungstic acid. Many of them produce slime in milk, especially at low temps.; this is due to the swelling of the capsules which surround the cells at certain stages of their life. *Streptococcus cremoris* also producedropy milk; this is the distinctive organism of the starters used in butter-making; its best strains apparently have the least power to ferment sucrose, maltose, and dextrin. When exptl. cheeses were made from practically germ-free milk inoculated with pure cultures of the lactic acid bacteria, putrefactive changes were greatly reduced.

JOSEPH S. HEPBURN

Comparative study of the two races of *Rhizopus nigricans*. GRACE A. DUNN. Johns Hopkins Univ. *Physiol. Researches* 2, 301-39 (1921).—Study was made of the growth of two sexual races of the fungus, *Rhizopus nigricans*, in 95 different nutrient solns., using the dry wt. of the fungus produced as a measure of the growth. The cultures were kept in the dark at a practically const. temp. (25° to 26°). Both races thrived excellently in a liquid medium containing  $\text{KH}_2\text{PO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{MgSO}_4$ ,  $\text{FePO}_4$ , and *d*-glucose in the proper partial concns. Ca apparently was not required if the medium contained the salts just mentioned, but  $\text{Ca}(\text{NO}_3)_2$  had no noticeable injurious action in the concns. tested with a fair physiol. balance of the other solutes. Neither the  $\text{NO}_3$  ion nor the  $\text{NO}_2$  ion had any notable influence on the growth, and neither was used as a source of N; however the  $\text{NH}_4$  ion of  $\text{NH}_4\text{NO}_3$  was used as a source of that element. The ions required for good vegetative growth and production of sporangia were: K,  $\text{NH}_4$ , Mg, Fe,  $\text{PO}_4$ , and  $\text{SO}_4$ . Glycerol could be used as a source of C, but was inferior to *d*-glucose. The activity of both races of the fungus was governed by a combination of (1) salt (or ion) proportions, (2) total salt concn., and (3) *d*-glucose concn. The highest rate of growth with both races was obtained with a nutrient soln. which (1) contained the following salts in the molecular proportions given:  $\text{KH}_2\text{PO}_4$ , 6,  $\text{NH}_4\text{NO}_3$ , 1,  $\text{MgSO}_4$ , 1.1,  $\text{FePO}_4$ , a mere trace, (2) had a total salt concn. equal to a calcd. osmotic pressure of 14.5 atm., and (3) had a *d*-glucose content of 1 gram-mol. per l. The wt. in gram-mol. of each compd. present in 1 l. of this soln. was:  $\text{KH}_2\text{PO}_4$ , 0.28,  $\text{NH}_4\text{NO}_3$ , 0.0462,  $\text{MgSO}_4$ , 0.0497,  $\text{FePO}_4$ , trace, *d*-glucose 1.0. No difference between the 2 races with respect to growth (total yield of dry matter) was noted when *d*-glucose was used as the source of C. When glycerol was used as the source of C, while the yield of both races was only of medium magnitude, yet the male race uniformly gave a markedly higher yield than the female race. In the solns. containing *d*-glucose, the male race produced sporangia more pronouncedly, while the female race produced mycelia more pronouncedly.

JOSEPH S. HEPBURN

Enzymes of *Bacillus coli communis*. V. (a). Anaerobic growth followed by anaerobic and aerobic fermentation. (b). Effects of aeration during the fermentation. E. C. GREY AND E. G. YOUNG. *Proc. Roy. Soc. (London)* 92B, 135-50 (1921); cf. C. A. 15, 246.—Anaerobic fermentation of glucose by an emulsion of *B. coli communis* proceeds differently according to the environment (aerobic or anaerobic) in which the microorganisms have previously been grown. When the immediate past history has been anaerobic, fermentation under anaerobic conditions produces very little or no lactic acid and a greatly decreased yield of succinic acid, while AcOH is produced in large amt. The formation of AcOH instead of succinic acid is additional proof of the close relationship of these 2 compds. The lactic acid, AcOH, and probably  $\text{CO}_2$  fermentations are independent of each other. Introduction of O during the fermentation increases the AcOH, lactic, and succinic acids, decreases the H,  $\text{CO}_2$ , and  $\text{HCOOH}$ , and has no influence on the yield of alc. The proportion of alc. to AcOH has a wider range under anaerobic than under aerobic conditions; apparently introduction of O during the fermentation inhibits the mechanism of auto-reduction which is responsible for variations



in the yield of alc. The products of aerobic fermentation of glucose contain less O than do the products formed on its anaerobic fermentation; but both sets of products contain more O than the original glucose. This extra O is probably derived from the water; and introduction of O apparently decreases the part played by water in the reactions.

JOSEPH S. HEPBURN

The bactericidal action of rabbit bile on certain strains of streptococci. R. L. STONE. Univ. California. *Proc. Soc. Exptl. Biol. Med.* 18, 34-6(1920).—All strains of *Streptococcus pyogenes* were killed by rabbit bile; non-hemolytic streptococci were unaffected; hemolytic, mannitol fermenting streptococci are almost always unaffected by rabbit bile. This action is unaffected by sterilization of the bile; it appears to be due to a substance present with or identical with a bile salt, being alc. sol. and pptd. by  $\text{Et}_2\text{O}$ . Other types of bile do not have this bactericidal effect.

V. C. MYERS

#### D--BOTANY

CARL L. ALSBERG

Plant colors. HENRY KRAEMER. *Am. J. Pharm.* 93, 414-16(1921).—A discussion of anthocyanin colors.

W. C. GAESSLER

Some experiments on the modification of color in plants. HENRY KRAEMER. *Am. J. Pharm.* 93, 416-8(1921).—Studies of changes of the color in flowers, the plant being in a fixed environment, is essentially a physiological study of the plant soil. Subsequent studies show that the pigment is distributed in four ways in the flower: (1) The pigments are usually in epidermal cells as in the rose and pansy. (2) The pigment may occur in sub-epidermal cells in addition as in wild hyacinth. (3) It may occur in the mesophyll layers in addition as in *Mertensia*. (4) It may occur in the conducting tissues surrounding the mestome strands in the flower as in blue hyacinth. From this study of the distribution of flower color substances it would seem, that if the study were made of those plants in which the pigment in the flowers was in the immediate proximity of the fibro-vascular bundles, that the chemical supplied the plant through the soil might be more or less unaltered and produce communication in the pigment cells.

W. G. GAESSLER

Composition of the velvet bean. E. R. MILLER. *Alabama Coll. Sta. Rept.* 1919, p. 34; *Expt. Sta. Record* 42, 801-2; cf. *C. A.* 15, 1152.—Data are reported on the compn. of the velvet bean (Early Speckled variety) as follows: Ash 2.8 to 2.9%, Ca 0.13 to 0.15, Mg 0.14 to 0.16, P 0.4, S 0.31, Cl 0.021, ether ext. 6.5, protein 20, carbohydrate (principally starch) 30, and alc. ext. 12 to 13%. The ash content of the stems and leaves of the plants collected when the fruit was mature was 2.96 and 11.9%, resp., and the corresponding figures for the plant in full bloom were 4.37 and 5.85%. The stems of plants in bloom contained 0.71% Ca and 0.319% Mg, and the leaves 1.433% Ca, 0.214% Mg, and 0.187% P. The results obtained from other varieties of velvet beans did not differ greatly from those of the Early Speckled variety. H. G.

Phytochemical investigations on indigenous and naturalized plants. I. J. A. DOMÍNGUEZ, J. F. MOLINO, AND E. L. DE CALLELLI. *Anales soc. quim. Argentina* 7, No. 29, 5-11(1919); *Expt. Sta. Record* 43, 820 1.—Preliminary studies are indicated as furnishing data for more specialized studies to follow regarding the content of numerous plants named in cyanoglucosides, saponins, alkaloids, oxidases, peroxidases, and other principles.

H. G.

Induced changes in reserve materials in evergreen herbaceous leaves. G. M. TUTTLE. *Ann. Botany* [London] 33, No. 130, 201-10(1919); *Expt. Sta. Record* 43, 29; cf. *C. A.* 15, 1334.—T has made a study of reserves, alterations therein, and related occurrences, mainly in *Linnaea borealis*. It is stated that in northwest Canada most evergreen plants are free from starch as early as October, when they are found to contain



a considerable amt. of oil. Exposure of *Linnaea* to higher temp. induces in darkness formation of starch which is present in about two days, increasing until about the eighth day. The starch is in a highly divided state, the individual grains exhibiting Brownian movement. Conversion occurs in all healthy leaves. Low temps. are dangerous to leaves filled with starch. The starch disappears after exposure for 8 days to moderately low temps. Starch formation is associated with loss of oil content. Enzymes are present in material undergoing conversion. Lipase has also been demonstrated in such materials. Oxidases are present in the leaf of *Linnaea* even at low temps. H. G.

The injurious effects of ultra-violet rays. A. URSPRUNG AND G. BLUM. *Ber. bot. Ges.* 35, No. 4, 385-402(1917); *Expt. Sta. Record* 42, 730.—A comparative study of the influence of ultra-violet rays on plants of several species is followed by a discussion of their relative resistances to the injurious effects of these rays, and the basis of such resistance, such as absorption of the rays by the epidermis. H. G.

Photochemical extinction during the process of assimilation. A. URSPRUNG. *Ber. bot. Ges.* 36, No. 3, 122-35(1918); *Expt. Sta. Record* 42, 730.—U. reports with discussion a study and the resulting data regarding the absorption of solar energy in different portions of the solar spectrum by leaves of different plants. H. G.

The supposed resistance of dry plant protoplasm to absolute alcohol, ether, and other anesthetics. A. RIPPEL. *Biol. Zentr.* 37, No. 10, 477-98(1917); *Expt. Sta. Record* 44, 28.—It is claimed that a supposed immunity to injury by pure alc., ether, and other anesthetics and by undiluted org. substances is not supported by the evidence obtained in these investigations. Cellulose and certain modifications thereof are, on account of their colloidal characters, deemed impermeable to such substances, so that the explanation of such immunity rests upon a purely mechanical basis. H. G.

The biochemistry of tobacco. II. Tobacco seeds. G. PARIS. *Bol. Soc. [R. ist. sci. sper. tabacco, Scafati]* 17, No. 1, 101-15(1920); *Expt. Sta. Record* 44, 201.—In continuation of the investigation previously noted (*C. A.* 11, 2598), a chem. examn. is reported of tobacco seeds with a view to their practical utilization. The chem. compn. of the entire seed is given as including water 9.17%, crude protein 21.87, fat 37.68, amides and sugar 6.05, pentosans 2.9, cellulose 7.15, and ash 3.84. The ash contained  $\text{SO}_3$  1.97%,  $\text{P}_2\text{O}_5$  22.12,  $\text{Na}_2\text{O}$  3.48,  $\text{K}_2\text{O}$  28.5,  $\text{CaO}$  9.54, and  $\text{MgO}$  14.63. On expressing the oil from the seeds by means of an hydraulic press a hard compact press cake, pulverizing with difficulty, was obtained of the following compn.: Water 11.83%, crude protein 28.63, fat 1.64, non-nitrogenous extractives 31.41, cellulose 19.9, and ash 6.5. Attention is called to the similarity in compn. of this press cake, except for its lower content in fat, to the press cakes of tomato and flax seeds. It is thought to be suitable as a *feeding stuff* or a *fertilizer*. The oil from tobacco seeds was of a light yellow color with practically no odor. The consts. of a sample of oil obtained from Kentucky tobacco seed were as follows: Sp. gr. (15°) 0.9408, temp. of solidification 12°, acid number 4, sapon. number 196, I number 132.8, and other number 192. The oil consisted of about 52.4% of olein, 22.1 of linolein, and 23.9 of palmitin. The oil is recommended as a drying oil as a substitute for linseed oil. Further study of the tobacco seeds consisted of an investigation as to the presence of nicotine and the nature of the nitrogenous constituents. No nicotine was found except in slight quantities in the germinating seed. The dry seed, from which the fat had been removed, was found to contain 6.5% total N, 3.76 protein N, 2.39 nucleic N, and 0.35 nonprotein N. Further examn. showed that the nitrogenous constituents include proteins sol. in water, in 10% NaCl, and in 0.5% KOH. The presence of arginine was detd. H. G.

The production of fat in plants. T. BOKORNY. *Botan. Centr., Beihefte* 35, Abt. 1, No. 1, 171-81(1917); *Expt. Sta. Record* 43, 430.—An account is given of the detn. of the production of fat in plants, particularly yeast in the presence of nutrients. H. G.



Physiological study of maple seeds. H. A. JONES. *Botan. Gaz.* 69, No. 2, 127-52 (1920); *Expt. Sta. Record* 44, 323.—The seeds of the sugar maple (*Acer saccharum*) and river maple (*A. saccharinum*) showed some striking contrasts, here detailed, as regards season of maturity, reaction to external conditions, chem. compn., and phases of physiol. behavior in general.

H. G.

The fermentation by some yeasts of nectar from winter plants. K. SCHÖGL-HORN. *Bul. soc. botan. Genève* [2] 11, 154-90(1919); *Expt. Sta. Record* 43, 730.—Particulars are given regarding the characters and fermentation of nectar from different plants.

H. G.

Mucilage or slime formation in the cacti. E. C. STEWART. *Bul. Torrey Botan. Club* 46, No. 5, 157-66(1919); *Expt. Sta. Record* 43, 226.—Having studied mainly in this connection *Rhipsalis rhombica*, S. reports that he has found in cacti a transformation in the content of many cells in the growing regions into mucilage, which by absorbing water, may simulate true growth and may be of importance in conserving and regulating the supply of water for the growing cells. Apparently the cell wall is not involved. The mucilage comes from the protoplasm and the formation begins between the cell wall and the protoplasm. As the mucilage increases, the nucleus and cytoplasm give way to it until it completely fills the enlarged cell. It is not held that all resins, gums, and mucilages are similarly formed. It is stated that the method of secretion here noted in connection with mucilage cells of the cacti is much more like that of the gland cells of animals than the more familiar method by a resinogenous layer of the cell wall as found in many trichomes.

H. G.

Nitrogen metabolism and yellowing in leaves of *Tropaeolum majus*. A. MEYER. *Flora [Jena] n. ser.* 11-12, 85-127(1918); *Expt. Sta. Record* 43, 729-30.—This deals with the color changes occurring in the life course of leaves of normal plants, the microscopic xanthoprotein reaction and coloration in living leaves, microscopic investigation of palisade cells in *T. majus*, the formation of nitrogenous materials in chloroplasts, and the influence of different factors in leaf coloration. Exact conclusions await further detns.

H. G.

The influence of cold in stimulating the growth of plants. F. V. COVILLE. *J. Agr. Research* 20, 151-60(1920); *Expt. Sta. Record* 44, 424-5. C. describes expts. and records observations on the effect of chilling during dormancy on the resumption of growth in some native species of trees and shrubs. It is claimed that such plants will not resume normal growth in the warm spring weather unless they have been subjected to a period of chilling. The effect of cold on dormant plants is believed to be intimately associated with the transformation of stored starch into sugar. In explanation C. suggests that the starch grains stored in the cells of the plant are at first sepd. by the living and active cell membranes from the enzyme that would transform the starch into sugar, but when the plant is chilled the vital activity of the cell membrane is weakened so that the enzyme leaks through it, comes in contact with the starch, and turns it into sugar.

H. G.

Cell growth in relation to supply of energy by protoplasts. J. M. JANSE. *Jahrb. wiss. Botanik* 58, No. 2, 221-36(1917); *Expt. Sta. Record* 43, 131-2.—This is an account of both the physical and chem. aspects of energy supply for cell growth.

H. G.

Uptake and anomalous osmotic coefficients of glycerol and urea. H. FITTING. *Jahrb. wiss. Botanik* 59, No. 1, 1-170(1919); *Expt. Sta. Record* 44, 223.—Following up the discovery that the isotonic coeffs. of a series of salts differed notably in certain connections from the expected values, F. has studied permeability in different plants, the results of which are detailed with discussion.

H. G.

Oxidizing power of roots of higher plants. R. BORKOWSKI. *Landw. Vers. Sta.* 94, 265-85(1919); *Physiol. Abstracts* 6, 100. Growing roots of higher plants possess



power of oxidizing Fe in dil. solns. The process is limited, on the root surface to the root hairs and the region between root cap and growing point; inside the root, to the walls of the vessels and adjoining parenchyma. In some plants the oxidizing power increases with age, while in others the reverse condition holds. The relation of this process to the various soil processes is discussed.

H. G.

**The biochemistry of resistance in disease in plants.** R. A. GORTNER. *Minnesota Sta. Rept.* 1919, 34, 35; *Expt. Sta. Record* 42, 841.—A brief report is given of investigations on the resistance of diseases in plants, the chem. compn. of plums resistant and nonresistant to the brown rot organism being studied. In addition, culture expts. with the brown rot fungus (*Sclerotinia cinerea*) were made on prune and apple juice media, and the expts. have shown that an active pectase is elaborated by the hyphae which causes the coagulation of sol. pectins into Ca pectate. If sufficient pectin is present, a fairly firm gel is produced upon which the fungus develops. It is claimed that when the fungus penetrates a host tissue, it dissolves out the middle lamella, but instead of assimilating it for food, the material is pptd. into a compd. of Ca pectate. This fills the intercellular spaces, and by preventing the collapse of the tissue, the infected fruit remains firm and retains its form. Through the presence of the Ca pectate in the dried mummies on the trees, water is imbibed freely, and this provides the dormant mycelium with a source of moisture that permits growth and formation of spores during blossoming time of the trees. Considerable culture work was done with this fungus to det. its fundamental nutrition, but all attempts to compound a synthetic medium that would support it have failed. It is believed that the juice of the host plant is necessary for the development of the fungus, and this suggests the existence of some accessory food substance which is present in natural hosts.

H. G.

**Excretion and its significance in life of plants.** K. GERHARDT. *Naturwissenschaften* 8, 41–3(1920); *Physiol. Abstracts* 5, 578–9.—Oxalic acid is formed in the plant for the removal of excess Ca. Guttation serves in the maintenance of the transpiration stream under conditions unfavorable for transpiration, but principally in removing excess salts. Where Ca oxalate is produced in guttating plants the crystals of the former (raphides) are protective against animal enemies. Silica and CaCO<sub>3</sub> may serve a similar purpose. Non-secreting plants (e. g., orchids) may form only a little pollen in consequence of poverty in nutrient salts.

H. G.

**Permeability in plant cells.** F. WEBER. *Naturw. Hochschr.* 33, No. 7, 89–95 (1918); *Expt. Sta. Record* 43, 821.—This is largely a synthetic and interpretative discussion of the data and conclusions of others regarding osmotic relations in plant cells.

H. G.

**Research work with range plants poisonous to stock.** M. R. MILLER. *Nevada Sta. Repts.* 1919, 32, 33; *Expt. Sta. Record* 43, 273.—Two plants, one of the saltbushes (*Atriplex canescens*) and the wild chokeberry (*Prunus demissa*), were investigated by M. during the year. The work with *Atriplex* disclosed the presence of a saponin or a mixt. of saponins to which it may be possible to ascribe some of the poisonous properties of the plant. *P. demissa* was shown to contain a cyanogenetic compd. The toxicity of this plant is undoubtedly due to the HCN generated by enzyme or other action.

H. G.

**Report of the department of chemistry.** T. O. SMITH. *New Hampshire Sta. Bul.* 192, 20–2(1919); *Expt. Sta. Record* 43, 29.—A brief report is made of cooperative work on the physiology of the apple, (cf. C. A. 15, 700) and an account given of studies of the relation of K to the growth of cereals. Wheat, corn, and buckwheat were grown in water and sand cultures, and it was found that all three species required a supply of K in addition to that stored in the seed itself within a few days after germination.

H. G.

**Root excretion.** J. K. GREISENEGGER AND K. VORBUCHNER. *Öster.-ungar. Z.*



*Zuckerind. und Landw.* 47, 82-91(1920); *Physiol. Abstracts* 6, 100.—The authors grew onion bulbs, from which roots began to appear after a day. The water into which the roots grew remained neutral to litmus, but  $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{Fe}^{III}$ ,  $\text{Mg}$ ,  $\text{Na}$ ,  $\text{Ca}$ ,  $\text{K}$ ,  $\text{P}$ ,  $\text{NO}_3$ , diffused into the water, as well as  $\text{NH}_3$ ,  $\text{CO}_2$ , glucose, and mustard oil. These results support the opinion of Brocq-Rousseau and Grain as to the existence of osmotically active secretions from roots.

H. G.

Experiments to test effects of iron salts on corn plants. G. N. HOFFER AND R. H. CARR. *Phytopathology* 10, No. 1, 57(1920); *Expt. Sta. Record* 44, 326.—In order to test the capacity of the tissues of cornstalks to accumulate  $\text{Fe}$  and other metallic base compds., 0.5, 1, and 2% solns. of various  $\text{Fe}$ ,  $\text{Cu}$ , and  $\text{Al}$  compds. were introduced in the stalks through punctures made in the internodal cortical tissues.  $\text{FeSO}_4$  solns. were active in affecting the nodal tissues. Catalase and oxidase actions were greatly increased and the tissues became brown and disintegrated, the leaves wilted and fired, and premature death of the stalks resulted. The effects of the treatments were similar to those observed in stalks affected by root rots. The ferric salts of equal concns. and quantities were either less effective or had no apparent effect whatever. In all cases ferric salts stimulated oxidase and catalase action but not to the same degree as the  $\text{FeSO}_4$  solns.  $\text{K}_2\text{SO}_4$  solns. had no noticeable effect.  $\text{Al}$  salts stimulated catalase and oxidase action, while  $\text{Cu}$  sulfate was very toxic. Check plants supplied with water or with nutritive salt soln. in equiv. concns. showed no harmful effects from the treatment.

H. G.

Anthocyanin of *Beta vulgaris*. F. M. ANDREWS. *Proc. Ind. Acad. Sci.* 1917, 167; *Expt. Sta. Record* 43, 132.—The anthocyanin of *B. vulgaris* affords one of the examples where the pigment forms in the subterranean parts. A strong soln. of such anthocyanin will preserve its normal color in a test-tube placed in darkness for more than a week. In direct sunlight it will retain its normal bright color for a week or more, until disorganized by bacterial action, which change finally occurs in the anthocyanin soln. in the dark.

H. G.

The synthesis of sugars from formaldehyde, carbon dioxide and water. A. J. EWART. *Proc. Roy. Soc. Victoria* 31, No. 2, 378-87(1919); *Expt. Sta. Record* 43, 202-3.—In continuation of work previously noted (C. I. 13, 1083), E. reports investigations on the polymerization of  $\text{CH}_2\text{O}$  to sugar by alkalis and alk. carbonates. "The main conditions for a high proportion of sugar are appropriate diln. and a temp. of 100 to 110°. The by-products are formates and  $\text{MeOH}$  namely. At low temps. little or no sugar is produced. The most rapid reaction is produced by  $\text{NaOH}$ . In the presence of a neutral  $\text{Ca}$  salt the amt. of sugar condensation is greatly increased, less alkali is required, and less formate produced. Neutral  $\text{Ba}$  and  $\text{Sr}$  salts are less effective as condensing catalytic agents. The best method is by running 7 to 8 cc. of 3.5%  $\text{NaOH}$  into 250 cc. of 0.8%  $\text{Ca}$  formate contg. 5 cc. of 40%  $\text{CH}_2\text{O}$ , while boiling in a condensing flask. The reaction is completed in a few minutes, and as soon as a pale yellowish tinge appears all the  $\text{CH}_2\text{O}$  has disappeared. The sugar mixt. is optically inactive, and contains reducing pentoses and reducing fermentable hexoses.  $\text{CO}_2$  and water are readily polymerized to sugar by the aid of  $\text{Mg}$ . The production of  $\text{Ca}$  tartrate [previously noted] during sugar synthesis has not been confirmed, and was possibly due to the use of an oxidized sample of  $\text{CH}_2\text{O}$ ."

H. G.

Presence of a phycoerythrin in the *Nostoc commune*. E. C. TEODORESCO. *Rev. gin. bot.* 32, 145-60(1920); *Physiol. Abstracts* 5, 579.—T. has succeeded in sepg. from samples of *Nostoc commune* a substance either identical with, or very little different from, the phycoerythrin of the red alga. The methods of abstraction and analysis are described.

H. G.

The jack bean. C. V. PIERCE. *U. S. Dept. Agr. Dept. Circ.* 92, pp. 12(1920);



*Expt. Sta. Record* 43, 233-4.—The plant is described, its history, botany, and culture are noted, and its value as green manure, green feed, hay, silage, and human food, and as a source of *urease*, a substance used in medicine, are discussed. The results of chem. analyses of the different parts of the plants, as compiled from various sources, are given in a table.

H. G.

The influence of light- and gravitational stimuli on the seedlings of *Avena sativa* when free oxygen is wholly or partially removed. U. P. VAN AMEIJDEN. *Verslag Akad. Wetenschappen Amsterdam* 25, II, 1135-43(1916-17); *Proc. Acad. Sci. Amsterdam* 19, II, 1165-73(1916-17); *Expt. Sta. Record* 42, 729-30.—Expts. were carried on with *A. sativa* seedlings under a total pressure of one atm. maintained by replacing removed O with N. Geotropic response was diminished by a fore period of 5 hrs. in N, and was absent after a fore period of 6 hrs. Phototropic response was apparently unchanged after 3 hrs. in N. It was still perceptible after a 6-hr. immersion, but after 8 hrs. in N it was entirely absent. When N was replaced by air after 65 or 75 min., a slight after effect began to be apparent about 1 hr. later, showing that so-called perception had occurred but that O was required to show a reaction. After a fore period of 24 hrs. in 4 to 5% O, the plants in ordinary air showed an influence on perception, the seedlings remaining able for a long time to perceive a geotropic or a phototropic stimulus in an atm. contg. a relatively low percentage of O.

H. G.

The identification of the sugar in the fruit of *Phytolacca dioica*. VICTOR ARREGUINE, JR. *Anales soc. quim. Argentina* 8, 229-32(1920).—The fully ripened fruits contain no reducing sugars. The sugar present is sucrose.

L. E. GILSON

The participation of the lipoids in the material exchange of plant cells. FRIEDRICH BOAS. *Biochem. Z.* 117, 106-214(1921).—B. studied the effect of saponin on the growth and activity of yeast in the presence of various salts. His results indicate that the compd. facilitates the fermentation of the important sugars by this organism on account of the bringing-about of an alteration in the colloidal conditions of the plasma lipid membrane in the sense of increasing the permeability. Those univalent and bivalent salts which show a sequential anion and cation series in their action on alcoholic fermentation practically coincide in their serial action on the lipoids, lecithin and better cholesterol. This salt action can then be attributed to an effect on the lipoids of the plasma surface.  $Al_2(SO_4)_3$  and  $Al(NO_3)_3$  inhibit fermentation in the concns. used (up to 0.005 M  $Al_2(SO_4)_3$ ). Saponin in combination with univalent or bivalent cations quickly suppresses fermentation if the salts are present in high concn. (0.2 N). This effect is suppressed by the addition of an oppositely acting cation in noteworthy amts. Acids also detoxicate the salt-saponin combination. Saponin and Al salts combined act as a stimulant to fermentation; perhaps the acid reaction is responsible. When non-electrolytes are combined with saponin its action is uninfluenced and this fact is taken as an expression of the general ineffectiveness of non-electrolytes in colloidal processes. These findings as a whole point to the idea of colloidal reactions in the plasma membrane and are indicative of an alteration in the degree of dispersion of the membrane lipoids. As far as the use of saponin is concerned it proves the participation of lipoids in cellular exchange; as far as the salt effect is concerned, the lipid participation is rendered probable. This conclusion is borne out in part by expts. with cells from higher plants. They also indicate that the idea that the plasma membrane is solely protein in nature is improbable. B. also exptly. refutes Swellengrebel's (*Centr. Bakt. Parasitenk. Abt.* 14, 378(1905)) report of  $CHCl_3CHO$  plasmolysis of yeast cells and attributes the early results to the use of non-living cells.

F. S. HAMMETT

The manganese content of seeds from Holland. D. H. WESTER. *Biochem. Z.* 118, 158-63(1921).—The Mn content of some 38 different kinds of seeds was detd. by the persulfate method. The results are reported in terms of dry material and ash. The



H<sub>2</sub>O content of the seeds was detd. by heating at 105–110°. The ash was obtained by incineration at red heat. The residue was taken up in HCl and evapd. to dryness on the water bath. The Cl was removed by heating with H<sub>2</sub>SO<sub>4</sub>. The author considers that no Mn is lost in this process and that heating once with H<sub>2</sub>SO<sub>4</sub> is insufficient to drive off all the Cl. In the majority of cases 2 to 6 mg. of Mn was found to be present per 100 g. dry matter. *Lupinus luteus* contained 1700 mg. Mn per 100 g. ash.

F. S. HAMMETT

**Chemical changes in wheat during germination.** H. A. CHOATE. *Bot. Gaz.* 71, 409–425(1921).—Marquis wheat (a hard spring variety) was used. Micro-methods (mainly qualitative) were employed. Ungermiated grains were soaked for 2 hrs. in distd. water to facilitate sectioning. For germinated material the grains were soaked for two hrs. and then placed in covered Petri dishes with moist filter paper on the bottom. These dishes were kept in a dark room at 16–20°. The dishes were opened daily and the air was renewed. The germination period was regarded as 7 days. The principal storage carbohydrate is starch in the endosperm. The first noticeable chemical change during germination is the appearance in the scutellum and coleorhiza of dextrin, and in the root cap of starch. Reducing sugar (probably all glucose) appears in the embryo after 18 hrs. in the germinator. Peroxidase and catalase are present in all parts of the grain both before and during germination. The amt. of catalase present increases during the first seven days at a rate corresponding to the rate of increase in the respiratory activity. During germination the protein content of the endosperm, except for that of the aleurone layer, decreases greatly. Microchemical analyses show the presence of amino acids in the ungerminated grain and their increase in amt. during germination. Amino nitrogen is absent until the fourth day of germination. Asparagine is the only form that was identified. This appears only in the root and coleoptile, accumulating in the latter in considerable quantity. BENJAMIN HARROW

**Anthocyanins and anthocyanidins. IV. Observations on: (a) Anthocyan colors in flowers, and (b) the formation of anthocyanins in plants.** ARTHUR ERNEST EVEREST AND ARCHIBALD JOHN HALL. *Proc. Roy. Soc. London* 92B, 150–62(1921).—Traces of the salts of various metals were added to decolorized solns. of violanin or cyanin chloride; Fe, Cu and Sn did not produce an immediate change in color, but a stable, full intense blue gradually developed. Na, Ca, and Mg did not cause a return of the color even on long standing; the presence of anthocyanin in the colorless condition was proved in every case by full regeneration of the colored oxonium salt on addition of acid. These and similar expts. led to the conclusion that the blue color in the fine blue complex Fe salts of anthocyanins is due to the reaction of the Fe with a phenol group (or groups), and the stability of the color in dil. soln. is due to the attachment of the metallic salt to the oxonium complex. The blue color in blue alkali or alkaline earth salts of the anthocyanins is due to a phenol grouping, and the lack of stability in dil. soln. is due to the inability of these salts to form stable complexes with the oxonium group. Probably all the anthocyan pigments form additive salts with FeCl<sub>3</sub>, in which the Fe salt is attached to the oxonium group; however, characteristic colors are formed only when suitably placed phenolic OH groups also react. The blue colors of flowers containing anthocyanins are due to either: (1) anthocyan phenolates of alkali or alkaline earth metals, or (2) complex anthocyan Fe salts. Study was made of a considerable number of plants, the flowers of which, in a fully developed state, are characterized by well-marked anthocyan colored petals. Buds were taken from the same plant at intervals until the fully developed flower was reached. In some cases anthocyan did not develop until light fell upon the petals, in other cases it was present before the bud unfolded; in nearly every case a stage was noted in which the petals were yellow or colorless, and contained substances which became yellow on exposure to NH<sub>3</sub>. A



number of flowers which contain only flavonols when fully developed, were examd., but no evidence was obtained of the intermediate formation of anthocyan. These results indicated that flavonols were formed before anthocyan. Buds of a red rose and of a medium colored mauve violet (Maggie Mott) of the largest size attainable before the appearance of any sign of anthocyan formation were crushed in warm alc. (approx. 95%), and the ext. was filtered after a short period of time. The pale yellow filtrate became colorless on addition of a small amt. of concd. HCl, and a deeper yellow on addition of  $\text{NH}_4$ . When a small amt. of Mg was added to the filtrate containing HCl, a clear pale red color developed gradually in the case of both the rose and the violet, while controls (without Mg) remained colorless. Hence the buds contained flavonol derivs. which would have developed into anthocyan colors, but no anthocyan had yet been formed. The paper is a reply to that of Shihata, Shibata, and Kasiwagi (*C. A.* 13, 581-2). The green pigments are shown to be mixts. of blue and yellow pigments.

JOSEPH S. HEPBURN

**Physiologic role of the anthocyanins.** STAN JONESCO. *Compt. rend.* 172, 1311-3 (1921).—Expts. were carried out with buckwheat and Blé de Bordeaux plants grown in darkness. When the plants reached a length of 3 to 5 cm. they were exposed to light, and after 48 hrs. insolation were found to be strongly colored bright red or violet-red by an anthocyanin. Plants were analyzed while brightly colored, also after remaining 6, 10 or 15 days in darkness, the results being shown in the following table in g. per 100 g. of dry matter. Columns 1 and 4 give results after exposure to 48 hrs. light, 2 and 5, after 6 days in darkness, 3 and 6, after 10 and 15 days in darkness for the grain and buckwheat resp.

	1	2	3	4	5	6
Glucosides.....	1.94	0.42	0.32	2.47	1.75	0.63
Reducing sugars ...	5.40	7.56	8.89	5.61	3.33	3.41
Nonreducing sugars	1.08	1.05	0.76	0.73	0.28	....
Starches .....	16.23	15.80	14.20	19.09	8.70	8.38
Celluloses .....	1.47	2.19	4.50	0.83	1.23	1.65

L. W. RIGGS

**Anaphylaxis in plants.** AUGUST LUMIÈRE AND HENRI COUTURIER. *Compt. rend.* 172, 1313-5(1921).—Four leaves of wild sorrel of approx. equal size were selected for observation. Into the petiole of 2 of these leaves was injected 0.01 cc. of horse serum. No action was observed during one month. One of the leaves having received the previous injection and a control leaf were each injected with 0.3 cc. of the same serum. No change until the 5th day when the leaf receiving the 2 injections began to wither and was completely withered by the 10th day. The control leaf remained normal. Of 3 hyacinths growing in the same pot, 2 received in the bulb 0.02 cc. horse serum. No change appearing after 3 weeks, one of the injected plants received 0.25 cc. of the same serum, and after 4 days wilting began which was completed in 11 days. The other plants remained normal. Similar results followed a test made on growing onion bulbs injected with monkey serum.

L. W. RIGGS

## E—NUTRITION

PHILIP B. HAWK

**A note on the relative activity of the fat-soluble accessory factor in cod-liver oil and butter.** S. S. ZILVA, AND MASATARO MIYURA. *Lister Inst. Lance* 1921, I, 323.—By the use of a quant. method of estn. of the fat-sol. accessory factor in cod-liver oil and butter it was found that the former was much more potent. This high potency is contained particularly in the crude preps. of cod-liver oil.



There is thus exptl. evidence of the efficiency of cod-liver oil in the treatment of rickets.

E. B. FINK

**The diet of well-to-do children.** R. McCARRISON. *Oxford. Lancet* 1921, I, 348.—The most common dietary faults among children of the well-to-do are deficiency of vitamins and excessive amts. of carbohydrates with low salt content, esp. Ca, when milk is overheated and vegetables are scanty. The effects of such faulty foods as observed exptly. on monkeys have been: Congestion and hemorrhage in the wall of the stomach and intestine; atrophy of the myenteron; degenerative changes in Auerbach's plexus; dilatations in various parts of the tract; increased tendency to intussusception; inflammations of the colon; bacterial infection; depressed functional activity of the intestinal glands. Continued subsistence on such diets may lead to intestinal stasis particularly in its effects on the neuromuscular control of the bowel. Secondly there may arise disturbances in the endocrine organs particularly the adrenal. E. B. FINK

**New experiments on the elimination of some amino acids through the urine.** W. BLUM. *Beitr. z. Physiol.* 1, 385-438(1920); *Physiol. Abstracts* 6, 67.—Expts. on the utilization of amino acids taken by the mouth. The amt. of the amino acid escaping in the urine was estd. by formol titration. In man, of a dose of 10 g. of glycine, 8.1% of the amino acid was lost in the urine; the loss was somewhat reduced (to 5.6%) if the glycine was taken in 10 hourly doses of 1 g. each. A young pig wasted 27% of 14 g. of glycine, an older animal lost only 7% of double the quantity. The horse was found to utilize glycine only to a very limited extent; *D*-alanine was completely utilized in the human body, but of an equal quantity of the racemic amino acid 12 to 17% was eliminated. H. G.

**Some recent contributions to the literature of vitamins, their disorders and harmonies.** L. M. POTTER. *Intern. J. Pub. Health* 1, 86-91(1920); *Expt. Sta. Record* 44, 62-3.—Attention is called to the apparent diversity of opinions and exptl. facts in recent contributions to the literature of vitamins and to the possibility of harmonizing some of these diversities. This is followed by a brief discussion of the principal lines of investigation of the vitamins, including their existence, specificity, stability, autogenesis, and practical importance. The literature of scurvy is then reviewed according to this outline. A list of 32 literature references is appended. H. G.

**Observations on the use of protein milk in an infant clinic.** A. D'ESPINE. *Intern. J. Pub. Health* 1, 34-5(1920); *Expt. Sta. Record* 44, 64.—Case reports are given of the successful use of protein milk in the treatment of infantile gastroenteritis. The protein milk, which is prepd. by replacing a l. of milk by the clot of casein which it produces, and mixing it very thoroughly with 500 cc. each of water and buttermilk, is said to have the following compn.: Protein 3, fat 2.5, lactose 1.5, and salts about 0.5%. In practice it has been found advisable to add from 3 to 5% of Soxhlet sugar (a mixt. of malt sugar and dextrin). It states that the protein milk should not be used as a substitute for mother's milk, nor is it to be recommended as a diet for a healthy baby, but it has proved of great value in cases of intolerance to cow milk. H. G.

**Lactic acid milk.** D. H. SHERMAN AND H. R. LOHNES. *J. Am. Med. Assoc.* 75, 921, 922(1920); *Expt. Sta. Record* 44, 64-5.—The authors discuss the merits of lactic acid milk in infant feeding, and describe two methods for its prepn. by means of which it is claimed that a product can be secured having 4 of the points of advantage which are emphasized for protein milk, namely a relatively high protein, a full fat, a fine curd during digestion, and a condensed food. In distinction from protein milk the lactic acid milk contains a higher content of lactose, nearly twice as much of the sol. salts, and less of the insol. salts of Ca and Mg. The beneficial effects of both protein and lactic acid milk are ascribed largely to the action of the lactic acid, which stimulates both gastric and intestinal digestion and helps to sterilize the intestinal contents. H. G.



**Metabolism of adolescents.** F. C. WRIGHT. *J. Roy. Naval Service* 6, 277-87 (1920); 7, 21-36 (1921); *Physiol. Abstracts* 6, 65.—These papers are mainly statistical, and relate to the intake and output of energy in boys in training-ships, and give valuable data which will interest those concerned in metabolism. They averaged 16 years of age, and the daily output approached 3,700 cal. per diem. The minimum daily intake recommended is 3,800 for boys from the ages of 13 to 14, and 4,100 for those from 15 to 16.

H. G.

**Further investigations in origin and separation of oxalic acid in human and animal organisms.** L. WĘGRZYŃSKI. *Księga pamiątkowa wyd. w. 25 roczn. Wyd. Lek. Łwow.* 1920, 157; *Physiol. Abstracts* 6, 67-8.—Endogenous oxalic excretion in fasting rabbits was 0.15 to 0.19 mg. per kg. per day. More oxalic acid was excreted on a diet of oats than on carrots, and glucose (30 g. per day) gave the large amt. of 2 mg. per kg. per day. Glucose was toxic to oat-fed animals, unless  $\text{CaCO}_3$  was also administered. In normal and leucemic men administration of 4 to 5 g. of benzene per day caused a rise in the oxalic acid excretion. There was also an increase when the flow of bile into the intestine was obstructed.

H. G.

**Accessory factors of growth and equilibrium.** E. ZUNZ. *Scalpel* June 19, 1920, No. 25, reprint, 10 pp; *Physiol. Abstracts* 5, 536.—An account of recent work on the part played in the growth and maintenance of animals and plants, and in numerous deficiency diseases, by important amino acids, hormones, and vitamins. The concluding sentences on the growth of tumors are suggestive of the part accessory factors may play there. From their expts. on yeast Sugiura and Benedict suggest that the favorable effect of Ra in such cases may be due to the partial destruction of accessory substances.

H. G.

**Vitamines.** W. D. HALLIBURTON. *Scientia* 27, 194-200 (1920); *Expt. Sta. Record* 43, 367.—This is a brief discussion of the nature and significance of the vitamins, with references to some of the recent contributions to the subject. Cf. C. A. 15, 2299.

H. G.

**Influence of light on the intermediary protein metabolism.** P. LIEBESNY. *Z. physik. diätet. Therap.* 24, 182-92 (1920); *Physiol. Abstracts* 6, 66.—In two dogs fed on a constant diet of horse tripe it was found that exposure to the ultra-violet rays from a mercury vapor lamp caused an appreciable reduction in the vol. of urine and in its total N, creatinine, and neutral S content.

H. G.

**Renal irritation in man from high-protein diet.** THEODORE L. SQUIER AND I. H. NEWBURN. *Arch. Intern. Med.* 28, 1-19 (1921).—Four patients with hypertension but without definite evidence of renal involvement were given a high-protein diet (100-200 g.) for periods of 2-3 weeks. After such feeding, the urines of all contained albumin and red blood cells, although both had previously been absent. After a return to a low-protein diet, both albumin and blood cells disappeared from the urine. In 3 of these patients, the enlargement and edema of the retina were increased by the high-protein diet. A similar expt. was performed on a patient with low blood pressure, but with an active nephritis as judged from clinical findings and the presence of albumin in the urine. The high-protein diet was followed by an increased albuminuria and the appearance of red blood cells. Two men, in whom the existence of a nephritis was discovered in the course of this work, ate large amts. of meat at 2 meals on one day. Albumin, which was absent before the expt., promptly appeared in the urine of both and red blood cells in one. A similar expt. upon 5 normal young men was followed by the appearance of red blood cells in the urine of all.

I. GREENWALD

**The metabolic and energy exchange of little pigs as determined by feeding experiments and analyses of the whole pig.** O. WELLMANN. *Biochem. Z.* 117, 119-39 (1921).—W. detd. the N intake and output of a series of little pigs during periods of



3 to 6 weeks and then detd. the dry matter,  $H_2O$ , fat, ash and N content of the entire individual animal used. Litter and sex controls were used. From the figures he obtained he calcd. the energy exchange, the values for which are given in tables. The N exchange is apparently well checked by the N content of the exptl. pigs as compared with their controls. It was found that the little pigs that were fed on milk of a low N content used up more energy in growing than did those which were fed on a milk of a bigger N content. W. concludes that 11.5 calories of available energy are necessary for the formation of 1 g. of org. material by young pigs. From the practical point of view, when it is desired to cause the animal to lay on meat, it is necessary to give not only sufficient protein, but also enough protein-free feed so that the energy demands of meat production do not surpass the protein destruction. F. S. HAMMETT

**Facilitation in intermediary carbohydrate metabolism.** H. STAUB. *Biochem. Z.* 118, 93-102(1921).—When glucose is fed the height of the rise of the blood sugar and the duration of the hyperglucemia are the factors detg. the course of the intermediary metabolism. A large increase and long duration of hyperglucemia indicate a lowered utilization capacity of the organism. Expts. are reported which show that after a 10-hr. fast there occurs an optimum assimilation capacity for glucose and that this tends to decrease with increase in the duration of the fasting period. Work was found to decrease the capacity of the organism to utilize sugar as did a pure fat-protein diet. These expts. demonstrate that under certain conditions the body has increased difficulty in maintaining an equil. between tissue and blood sugar. This implies the presence of a facilitation process for the attainment of the equil. The facilitation for carbohydrate assimilation is explicable on the basis of an activating influence of the ingested carbohydrate or original glycogen stores on the enzymatic processes of the sugar complex. Carbohydrate assimilation itself induces a condition in the mechanism of carbohydrate metabolism which tends to produce a good utilization capacity. The relation of this principle to diabetes is briefly discussed. F. S. HAMMETT

**Chemical factors in nutrition.** LAFAYETTE B. MENDEL. Yale Univ. *J. Franklin Inst.* 192, 1-10(1921).—A discussion of recent advances in the chemistry of digestion and metabolism. JOSEPH S. HEDBERG

**The coming nutrition of peace times.** M. RUNER. *Z. öst. Fortbild.* 17, 273-8 (1920); *Physiol. Abstracts* 5, 472(1921).—The different *per capita* consumption of protein, fat, and total calories in various countries is due to differences in the distribution of the inhabitants between town and country. Sedentary town dwellers require a higher % of protein in the diet, since their environment causes a loss of appetite. The shortage of protein among the town dwellers of Germany during the war caused them to suffer a mean loss of wt., to compensate which will now require almost 300,000 extra tons of protein. JOSEPH S. HEDBERG

**Changes in organ weight produced by diets deficient in antiscorbutic vitamin.** V. K. LA MER AND H. L. CAMPBELL. Columbia Univ. *Proc. Soc. Exptl. Biol. Med.* 18, 32(1920).—Young guinea pigs weighing 250-300 g., fed on a diet deficient in  $H_2O$ -sol. C, show at death a pronounced increase in wt. of the adrenal glands, this may indicate a compensatory response to the decreased adrenaline production known to exist in the scorbutic animal. The heart and kidneys appear to be increased in wt. on scorbutic diets, while the liver shows no effect. V. C. MYERS

**Organic foodstuffs with a specific action.** F. ABDERHALDEN. *Arch. ges. Physiol.* 178, 260-308(1920).—Polyneuritis in pigeons was induced by continuous feeding upon polished rice, and the therapeutic effects of various fractions of yeast were measured. The results are tabulated in detailed protocols. In general, it appears that the "ultra-mine" of dried yeast can not be completely extd. by abs. alc., by acetone, or by a combination of these two extractives. The exts. of yeast given to pigeons on a rice diet



ameliorate certain symptoms of the disturbance but they fail to provide a complete regimen. Obviously there is some substance, insol. in nature, in the yeast which is effective in combating the disturbances associated with a polished rice diet. G. H. S.

**Calcium and phosphoric acid metabolism resulting from the administration of large amounts of calcium and sodium phosphate.** K. BLÜHDORN. *Z. Kinderheilk.* 29, 43-55(1921).—Large amts. of Ca, as  $\text{CaCl}_2$  or Ca lactate and of  $\text{Na}_2\text{HPO}_4$  were given children and the extent of elimination was detd. The large amts. of Ca caused no ill effects, no increase in diuresis, diarrhea was not induced, nor was there any loss in wt. In some instances a marked gain in wt. occurred during the expt. A portion of the excess of Ca given was retained, although the greater part was eliminated in the feces. The  $\text{P}_2\text{O}_5$  changes in general paralleled the Ca changes; a change in the Ca balance being accompanied by a corresponding change in the  $\text{P}_2\text{O}_5$  balance. G. H. S.

#### ABNORMAL

**Beriberi and deficiency diseases.** A. SCALA. *Ann. igiene* 29, 215-30, 286-301 (1919); *Expt. Sta. Record* 43, 462.—S. presents a critical discussion of the literature of deficiency diseases, from which he advances the hypothesis that they originate in a deficient mineral nutrition either in the lack of certain acids or bases or of complexes by means of which they are transported. In scurvy the inorg. substance which is lacking is thought to be the phosphates of the earth metals, which exist in food materials in combination with org. material in the form of complexes, easily decomposed by heat and by desiccation. The destruction of these complexes tends to bring about a state of acidosis and prevents the transportation of Ca phosphate, etc., to the bones. In beriberi the alk. phosphates are unable to reach the central nervous system through the destruction of the org. complexes contg. them and the development of a form of acidosis. The fact that various mineral substances when added to a beriberi-producing diet fail to bring about appreciable benefit is explained on the ground of inability to reproduce the exact complexes found in the original food material. H. G.

**Calcium metabolism and the teeth.** C. F. RUMSEY. *Brit. Dental J.* 42, 49-54 (1921); *Physiol. Abstracts* 6, 66-7.—The incidence of caries is complex, and diet a most important factor; the following subjects are dealt with: (1) Milk is the ideal Ca-contg. food, and should be relied on during the growth period; (2) bread should be made so as to contain more cellulose and more vitamins; (3) among fats, olein is preferable to the more solid fats; (4) Ca intake should also be regulated in adults, and symptoms of thyroid abnormality should be recognized and treated. H. G.

**Critical study of recent work on the pathogenesis of pellagra.** V. BABES. *Bull. sec. sci. acad. Roumaine* 6, 138-48(1920).—Recent researches have not been of a nature to clarify either the etiology or the pathogenesis of pellagra. They have only increased the uncertainty by new hypotheses, by misinterpretation of facts, and by poorly executed work which will pass into oblivion. The following facts concerning pellagra have been established: (1) The close relationship of the disease with the eating of maize, especially unwholesome maize. (2) The predisposition produced by inanition, weakness, congenital deterioration especially of a nervous type, certain diseases, and convalescence from these diseases. (3) The specific nature of pellagra. (4) The favorable action of an abundant mixed diet and the administration of atoxyl.

JOSEPH S. HEPBURN

**Comparative calorimetric studies of fasting and avitaminosis.** P. NOVARO. *Patologica* 12, 133-56(1920); *Physiol. Abstracts* 5, 555(1921).—When pigeons are kept on a ration of polished rice, the heat loss, food intake, body wt., and body temp. remain const. for a period of 7 to 13 days, then decrease in the order in which they were mentioned. The decrease in body wt. is more rapid than in fasting; and the heat loss in



the premortal state is very low, while it rises in fasting before death. Hence heat production is lessened before death from beriberi. When vitamins are administered at a late stage, the loss of heat becomes greater, and the body temp. rises, but the body wt. continues to decrease until the food intake is again adequate. JOSEPH S. HEPBURN

**Experiments on carbohydrate metabolism and diabetes. I. Intravenous glucose tolerance of dogs.** FREDERICK M. ALLEN AND MARY B. WISHART. Rockefeller Inst. *J. Biol. Chem.* **42**, 415-58 (1920).—Interrupted injections of glucose into the jugular vein were given to dogs, the expts. being started 20-24 hrs. after the last feeding. Special precautions were taken to prevent fright, pain or shock and only sturdy, phlegmatic animals accustomed to the lab. were used. The samples of blood were removed just before the injections so that the blood sugar values represent the minimum because taken at the end of the interval. In general the animals were catheterized hourly. In normal dogs a dosage of 1 g. per kg. per hr. is slightly above the tolerance limit. Variations in the concn. of the solns. injected have no perceptible effect upon the assimilation. In diabetic animals there is in general a reduction of tolerance as shown by the sugar excretion but this general rule is subject to very marked exceptions and sugar excretion is seldom an accurate measure of the degree of diabetes as known from the food tolerance and general clinical condition. The correct interpretation of the results depends on the detn. of the concn. of sugar in the blood as the amt. of sugar excreted in the urine is dependent upon the renal threshold for sugar of the individual animal. The lowered tolerance of the diabetic animals or those near to diabetes is indicated by their greater hyperglucemia. "The combined consideration of the glucosuria and the blood sugar concn. makes the intravenous method sufficiently accurate for practical tests of tolerance, and it holds a position of special usefulness in excluding irregularities of absorption, notably in such conditions as thyroid and pituitary deficiency. Outside of such special conditions, other factors seem to predominate over any possible irregularities of absorption, and it is doubtful if the intravenous method can show the finer gradations of tolerance such as are revealed by the alimentary or subcutaneous administration of glucose. Any lowering of assimilation demonstrable by the intravenous method in these expts. was fully obvious in feeding tests." Expts. were also conducted to det. the influence of fat and protein feeding upon the assimilation of sugar after intravenous injection. No evidence was obtained of a direct participation of the pancreatic hormone in protein or fat metabolism but the decisiveness of the expts. is open to question.

A. P. LOTHROP

**Experiments on carbohydrate metabolism and diabetes. II. The renal threshold for sugar and some factors modifying it.** FREDERICK M. ALLEN AND MARY B. WISHART. *J. Biol. Chem.* **43**, 129-47 (1920); cf. preceding abstract.—"A diminished renal permeability for glucose, in the sense of a raised threshold according to tests with Benedict's Cu soln., is definitely proved as the rule in diabetic animals. As the same rule holds for the great majority of human diabetics, this demonstration furnishes one more point of similarity between the exptl. and clinical conditions. Various possible causes for the elevation of the threshold are discussed. The prolonged excess of sugar in the blood may be an important factor, but some considerations seem to oppose it. Certain observations suggest that high-fat diets may raise the sugar threshold in diabetes even without acidosis. The renal threshold may be affected by various extraneous causes, of which the elevation of the threshold by epinephrine is one interesting example. No interrelation of the renal and pancreatic functions is demonstrable in the sense of an increased readiness of sugar excretion even in totally depancreatized animals. An elevation of the threshold seems to be connected particularly with severity of the diabetes but a teleological interpretation of this as a protective mechanism for saving sugar to the body is considered improbable."

I. GREENWALD



**Processes of sugar elimination in diabetes.** O. SCHMIDBERG. *Arch. exp. Path. Pharm.* 90, 1-26(1921).—An analysis is presented of the processes of sugar elimination in various forms of exptl. and pathol. diabetes. Glucose is one of the compds. that is easily and completely utilized; by the normal organism extremely large amts. can be taken care of without difficulty. In chronic glucosuria, or true diabetes, the normal processes are deranged, owing either to an impairment of the oxidation processes or to an incombustibility of the glucose. Even in the most severe cases of diabetes the oxidation processes of the body are entirely unchanged, thus the glucosuria in diabetes must result from a failure on the part of the glucose to be changed, and this failure can not be ascribed to cessation of the mechanism of glucolytic cleavage. In  $\text{CO}_2$  diabetes the non-combustion of the sugar is associated with the presence of a nitrogenous diabetogenic substance with which the sugar unites. This diabetogenic substance is undoubtedly a component of body protein. In diabetes of this type the liver certainly plays a part, for after exclusion of the liver from the circulation or after destruction of hepatic tissue  $\text{CO}_2$  intoxication does not lead to glucosuria. It may be that the diabetogenic substance is formed within the liver. In pancreatic diabetes, however, it is obvious that another factor is concerned, as is also true for diabetes mellitus. In these two conditions it would appear that some enzyme had been removed, and that the diabetogenic substance and the sugar, deprived of some inhibiting factor, were free to unite. Hyperglucemia is not the cause of diabetic glucosuria but is a consequence of this lack of transformation of glucose. Glucosuria may be present without hyperglucemia, and hyperglucemia may occur without sugar elimination in the urine. Since the glucose in diabetic urine is probably present in an unaltered state it must have become incombustible through union with some incombustible substance, which must make it incapable of transformation into glycogen. Adrenaline diabetes is apparently a form of pancreatic diabetes due to the action of the drug upon the ferment-producing property of the pancreas. The nature of phlorizin diabetes is yet to be detd.; it may be renal or perhaps pancreatic in nature. G. H. S.

## F—PHYSIOLOGY

ANDREW HUNTER

**Alpinism.** JOSEPH BARCROFT. London. *Lancet* 1921, I, 1277-9.—The effects of high altitudes manifest themselves first in a reduction in the amt. of  $\text{O}_2$  in the blood and then in the tissues. At sea level only 5% of the hemoglobin does not function. With rising altitude, a gradually increasing amt. of hemoglobin is deprived of its function because of the diminution of  $\text{O}_2$  in the air. At rest the  $p_{\text{H}}$  of the blood remains quite const. even with  $\text{O}_2$  want, but at high altitudes a much smaller amt. of exercise will produce the same changes as at low levels. The skeletal muscles easily become stiff from exercise. E. B. FINK

**Influence of oxygen pressure on the oxidation products of animal tissues and of oxidizing enzymes.** F. BATELLI AND L. STERN. *Compt. rend. des séances soc. phys. hist. nat. Genève* 37, 31-3(1920); *Physiol. Abstracts* 6, 48-9.—In general the oxidation processes increase with increased O pressure. Respiration expts. gave irregular results, but the respiratory quotient decreases with increase of O pressure. O pressures up to 4 atm. were used. H. G.

**Chemical-biological researches on lactic acid of the gastric juice.** U. MASUCCI AND P. SACCARDI. *Folia med.* 6, 97-100, 127-32(1920); *Physiol. Abstracts* 6, 54.—By the use of the resorcinol test (details recorded) the authors find that the lactic acid of the gastric contents is not the product of an enzyme action on any constituent of the food, but is formed in the cells of the gastric mucous membrane under the influence of the vagus. H. G.



**Pancreas function.** E. MEYNER. *Med. Klinik* (Vienna) 16, 678-80(1920); *Physiol. Abstracts* 5, 552.—Duodenal contents were collected by the Einhorn tube, and indications were found that the secretion there is not continuously, but rhythmically formed. The enzyme content in it varies considerably; food or fasting is one factor; reaction is another; it and the quantity of juice are highest when HCl is given, lowest when  $\text{NaHCO}_3$  is given. An acidity of gastric juice may thus produce diminution of pancreatic activity.

H. G.

**Physical-chemical mechanism of muscle contraction.** E. HERZFELD AND R. KLINGER. *Naturwissenschaften* 8, 359-63(1920); *Physiol. Abstracts* 6, 21.—The action current of the nerve decomposes the hexosephosphates, and the lactic acid so liberated is absorbed by the proteins of the muscle fibrillae, and so produces the contraction. The oxidative removal of the lactic acid brings the muscle into the resting condition once more.

H. G.

**Menstrual blood.** M. STICKEL AND B. ZONDEK. *Z. f. Geburtshilfe und Gynäkol.* 83, 1-26(1920); *Physiol. Abstracts* 6, 78.—No influence could be detected on the blood corpuscles and on their hemoglobin content in the whole blood during menstruation. The menstrual blood shows an oligocythemia and leucopenia. The color index is not reduced in proportion, because partial hemolysis of the uterine blood occurs. In the whole blood the lymphocytes increase during menstruation, and especially in the uterine blood. The total solids, and also their mol. concn., are diminished in the menstrual blood. No changes in the toxicity of the red cells and percentage of proteins were found. Hemolysis is probably the effect of an enzyme from the uterine mucous membrane. No changes of coagulation were observed in the whole blood, but menstrual blood does not clot. This inhibition of coagulation is also caused by a substance in the mucous membrane. Blood obtained by puncture of the uterus during menstruation clots normally. Apparent blood clots in menstrual blood are caused by sedimentation of the blood corpuscles.

H. G.

**Lipoids of the prostate.** M. KINOSHITA. *Z. Urol.* 14, 145-67(1920); *Physiol. Abstracts* 5, 559.—Lipoid granules, not doubly refracting, are found in the epithelial cells of the prostate from puberty to about 50 years of age, after which the amt. diminishes, although in old age doubly refractile droplets appear. Inflammatory changes cause diminution of the lipoids.

H. G.

**The relation between the adrenal cortex and sexual development.** KNUD H. KRABBE. *N. Y. Med. J.* 114, 4-8(1921).—After discussing the literature in its relations to the problem expressed in the title K. concludes that the development of pubic hair and beards in little girls with adrenal cortex tumors cannot be regarded as a special sign of precocious puberty, but must be considered as a natural link in hypertrichosis. This hypertrichosis, the development of a large clitoris and transformation of the voice in little girls are only to be considered as a virilism analogous to the virilism in adult women suffering from adrenal cortex tumors and the so-called fetal virilism in females with adrenal hyperplasia. There does not seem to be sufficient basis for the idea of a special connection between the normal function of the adrenal cortex and the sexual organs. A better explanation is based on the supposition that the cortex tumors have developed from the testicular part of the ovarian gland in connection with the anlage of the adrenal cortex in the fetal stage.

F. S. HAMMETT

**The problem of the adrenals.** E. GLERU. *N. Y. Med. J.* 114, 9-11(1921).—The problem of the adrenal function is considered as unsolved as yet by G.

F. S. HAMMETT

**The amino-acid content of the plasma and of the blood corpuscles according to I. Bang.** A. CONSTANTINO. *Biochem. Z.* 117, 140-4(1921).—The work of Bang (*C. A.* 10, 924, 2762) on the amino-acid N distribution in the blood fails to give C. proper



credit for the establishment of differences in the amino-acid content of serum and white and red corpuscles under various conditions (cf. C. A. 8, 2745). F. S. HAMMETT

**The fate of some polysaccharides in the digestive tract of mammals.** TOMIHIRO SHIMIZU. *Biochem. Z.* 117, 227-40(1921).—S. detd. the action of fecal material and fermentative bacteria on inulin, lichenin and hemicellulose. It was found that there is a substance in feces, probably a microorganism, which splits these polysaccharides to active propionic and butyric acids. Notable amts. of optically inactive lactic acid also are produced. Among the specific bacteria studied, *B. lactis* preferably forms acetic acid. *B. lactis*, *B. proteus*, *B. subtilis* and *B. coli*, besides forming the acids named above, produce optically active lactic acid, the first 3 yielding the dextro form and the last the levo form. The conclusion is made that inulin, lichenin and hemicellulose are split into sugars by bacteria in the digestive tract and absorbed. The splitting of some polysaccharides (inulin, lichenin and hemicellulose) in the digestive canal of mammals. *Ibid* 240-4.—When these polysaccharides are digested *in vitro* with exts. of macerated intestine and pancreas in 0.8% NaCl soln. no monosaccharide could be found either by the phenylhydrazine or the Fehling reduction test. This is taken to prove that there are no enzymes in such preps. capable of splitting inulin, lichenin or hemicellulose. The influence of some polysaccharides (inulin, lichenin and hemicellulose) on protein balance. *Ibid* 245-51.—In this paper S. reports the results of his study of the N equil. of a dog when fed inulin, lichenin and hemicellulose for several periods of three days each, with appropriate preliminary and post-feeding periods of observation. The total starch content of the feces was detd. All values are reported in extensive tables. The addition of either of the 3 carbohydrates to the meat diet resulted in a diminution of the N output. These polysaccharides then are digestible and available foodstuffs in the digestive canal of the dog and are protein spacers. The exact portion of the tract or the mechanism whereby they are split is not known.

F. S. HAMMETT

**Variations in chloride metabolism during menstruation.** W. EISENHARDT AND R. SCHAEFER. *Biochem. Z.* 118, 34-8(1921).—Studies of the Cl content of blood before, during and after the menstrual period demonstrate that marked changes occur. One or two days before the onset of menstruation or in the first two days of the period there is generally an absolute and relative hyperchloremia. When menstruation ceases the blood Cl falls back to the normal value. These phenomena were observed in two cases of transitory amenorrhea at the menstrual period. It is considered that the reaction is factored by endocrine disturbances possibly of the thyroid and ovary, as well as by the loss of blood.

F. S. HAMMETT

**The secretion of sweat and the composition of the blood.** FERHARD WILBRAND. *Biochem. Z.* 118, 61-6(1921).—In a series of personal studies W. found that excessive perspiration results in an increased concn. of the blood. When 25% of the H<sub>2</sub>O of the blood has been lost collapse occurs. The amt. of H<sub>2</sub>O removed from the blood increased with the increase in perspiration. H<sub>2</sub>O is also largely lost from the tissues, the NaCl and serum protein diminish during sweating and the diminution runs parallel with the degree of H<sub>2</sub>O loss. Man has the property of retaining NaCl in the tissues even when the salt is being lost from the blood. The fat and rest-N content of the blood are not significantly disturbed when sweating is induced.

F. S. HAMMETT

**Contribution to the question of the precipitation velocity of the red blood corpuscles of human blood.** KJ. VON OERTINGEN. *Biochem. Z.* 118, 67-92(1921).—The expts. reported by O. indicate that there is an acceleration of pptn. of the red blood corpuscles in pregnancy. The primary cause for this facilitation lies in the liquid material of the blood. This is supported by the dependence of the pptn. velocity on the properties of the medium, as well as the retardation of the reaction by increased salt content and



lowed temps. In blood from pregnant persons the pptn. velocity decreases with decrease in the corpuscle number within certain limits. When the ppt. obtained by treating plasma from pregnant women is added to blood from the umbilical cord, the latter is invested with an accelerating action on the pptn. of the corpuscles. The difference in reaction between gravid blood and blood from the umbilical cord is also exhibited in defibrinated blood in which the absolute pptn. time is lessened. O., therefore, concludes that these differences are not due to an increase or decrease in any particular protein constituent of serum, but that they are factored by the physical structure of the blood proteins; the solvent is, therefore, of great importance, and the stability of the blood plasma is considered as the primary cause of the differences observed.

F. S. HAMMETT

Respiration studies on new-born animals. RAHEL PLAUT. *Z. Biol.* 73, 141-150 (1921).—P. studied the respiratory exchange on new-born dogs, cats, rabbits, guinea pigs and mice. All detns. were made at the nest temp. The course of the O consumption curve is practically the same for all animals. There first occurs a rise to a max. This is followed by a drop, which is succeeded by another rise. This is slower than the first. In mice the O utilization proceeds without remission for the first 10 days. F. S. H.

Tables, factors, and formulas for computing respiratory exchange and biological transformations of energy. THORNE M. CARPENTER. *Carnegie Inst. Pub.* 303, 1-123 (1921).—A set of 33 tables with descriptions and directions for their use. "The purpose of this publication is to make available to investigators the majority of tables and conversion factors needed in calcs. of results from measurements obtained by the several types of respiratory exchange app., particularly the Regnault-Reiset and the combination of spirometer, valves, and breathing appliance, and to make available the standards of normal metabolism."

JOSEPH S. HEPBURN

Endocrinology: Thymus gland. AUGUSTUS KORNDORFER, JR. *Homeopathic Recorder* 36, 239-53 (1921).—A discussion of the internal secretion of the thymus gland, and of the part played by it in health and in disease.

JOSEPH S. HEPBURN

Physical and chemical properties of horse semen with special reference to the physiology of the spermatozoa. JINSHUN YAMANE. *J. Coll. Agr. Hokkaido Imp. Univ.* 9, 161-236 (1921).—Twelve samples of semen were collected on different days from each of 2 stallions; and the total solids (T. S.) and sp. gr. (at 18°) were detd. on each sample. With stallion 1, the sp. gr. ranged from 1.0100 to 1.0142, av. 1.0118, the T. S. from 1.7860 to 3.6230, av. 2.5903%; with stallion 2, the sp. gr. ranged from 1.0108 to 1.0155, av. 1.0127, the T. S. from 2.1741% to 3.7827%, av. 2.9553%. Samples from several other stallions also were examd. The variation, with respect to sp. gr. and T. S., in semen from the same animal on different days was greater than the variation in semen from different animals. Samples taken from the same animal on successive days showed a decrease in both sp. gr. and T. S., but an increase in both occurred if several days were then permitted to intervene between successive samples. By centrifugation the spermatozoa were removed and a serum was obtained. Eleven samples of this serum from stallion 1 had a sp. gr. ranging from 1.0099 to 1.0138, av. 1.0112, and contained from 1.6417% to 3.3258% T. S.; 11 samples from stallion 2 had a sp. gr. between 1.0106 and 1.0143, av. 1.0121, and contained from 2.1506% to 3.4216% T. S. The T. S. derived from mixed specimens of this serum contained, on the av., 37.719% ash in the case of stallion 1, and 34.443% ash in the case of stallion 2. The ash was pure white, partly sol. in water, completely sol. in HCl and HNO<sub>3</sub>, and contained Na, K, Ca, Mg, Cl, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, and CO<sub>2</sub>; the ratio of K to Na was 1.25, Ca to Mg 3:1, P<sub>2</sub>O<sub>5</sub> to CaO 1:1. This serum contained mucin, globulin, albumin, proteoses, and ether ext., but no sugar; its titratable alkalinity (methyl orange being used as an indicator) lay between 0.081 and 0.155% NaOH in 11 analyses on stallion 1, and



between 0.081 and 0.144% NaOH in 14 analyses on stallion 2. Daily ejaculations decreased both the total N and the alkalinity of the serum. The depression of the f. p. of the serum lay between 0.57° and 0.64° (av. of 11 detns. 0.608°) for stallion 1, and between 0.58° and 0.67° (av. of 11 detns. 0.623°) for stallion 2. The serum failed to yield the crystals characteristic of this fluid with either picric acid or I plus KI. The sp. gr. of the *spermatozoa* lay approx. between 1.096 and 1.099. They contained (2 analyses) 19.358% to 21.152% T. S.; they contained 8.813% to 9.108% ash (3 analyses), including Ca, Mg, K, Na, Fe, Cl, SO<sub>4</sub> and P<sub>2</sub>O<sub>5</sub>. The ratio of Mg to Ca was 1:2.7, CaO to P<sub>2</sub>O<sub>5</sub> 1:6.5. An *abnormal semen* from a stallion was unusually viscous, contained from 2.747% to 3.178% T. S., and was characterized by gelatinous masses and calculi. The calculi had a protein-like base and contained salts, especially carbonates and phosphates, of Ca and Mg. A sample of *ass semen* had a sp. gr. of 1.0167, and contained 4.2829% T. S. The following contributions are made on the *physiology of the spermatozoa*. A soln. isotonic for the spermatozoa had a f.-p. depression of 0.62°; they lived longest and had the greatest motility in a 6% glucose soln., which has this f.-p. depression. The action of NaCl was more unfavorable to duration of life and activity in an isotonic concn. than in a hypotonic concn., on account of the action of the ions. Agglutination of the spermatozoa was entirely independent of changes in the osmotic pressure, and was not produced by non-electrolytes (glucose, sucrose, urea), but was produced by NaCl. Alkali in low concns. was more favorable than a neutral soln. for prolongation of life of the spermatozoa, but was less favorable for retention of their max. motility. Na<sub>2</sub>HPO<sub>4</sub> in a concn. greater than 0.005 molar exerted an injurious action, but agglutination occurred only when the concn. of that salt was at least 0.02 molar. A soln. with an acid reaction always had an injurious action on the span of life and on the retention of max. motility; these effects became more marked, as the concn. of the acid increased. In low concns. of acid, the motility was stimulated to a max., then a paralyzing action was exerted. NaH<sub>2</sub>PO<sub>4</sub> produced agglutination in all concns.; and both the intensity of agglutination and the time required for its appearance were functions of the concn. of that salt. Univalent ions decreased the life span of the spermatozoa more than did bivalent ions; the action of the Cl ion in decreasing the life span was greater than that of the SO<sub>4</sub> ion, while the cations fell into the following order Li>K>Na>Ba>Ca>Mg>Sr. Motion was stimulated to a greater extent by Cl than by SO<sub>4</sub>; the univalent cations, except Li, stimulated motion, the bivalent cations tended to check it. In the production of agglutination, the ions fell into the following order Ba>Sr>Ca>Mg>K>Na>Li for the cations, and SO<sub>4</sub>>Cl for the anions; however, the cations were of primary importance, while the anions exerted but a slight influence. The specific action of a single salt upon the life span and activity of the spermatozoa was modified by the addition of another salt; and the action of this mixt. was further modified by the addition of a third salt. No noticeable antagonistic action of the salts occurred in agglutination, this phenomenon being governed by the bivalent ions. The serum obtained from the semen apparently was a soln. with antagonistic salts in physiological equil. with respect to the influence on the span of life and the activity of the spermatozoa. The osmotic pressure had no influence in the production of agglutination, since it was produced by electrolytes but not by non-electrolytes. Agglutination was favored by the H ion in all concns., by the OH ion only in definite concns. The period of time required for the beginning of agglutination, and the degree of agglutination were a function of the concn. of the electrolyte. Motility was a prerequisite for agglutination; spermatozoa, which had died or had been killed by reagents such as HgCl<sub>2</sub> or OsO<sub>4</sub>, would not agglutinate under the conditions which produced that phenomenon in living spermatozoa. Agglutination was found to be reversible; it was not specific for animal species (thus spermatozoa of both the rabbit and the horse



agglutinated into the same clump), and was not a simple flocculation, but was a positive chemotaxis of the spermatozoa for each other under the influence of electrolytes. A bibliography is appended.

JOSEPH S. HEPBURN

**Energy involved in the electric change in muscle and nerve.** A. V. HILL. *Proc. Roy. Soc. (London)* 92B, 178-84(1921).—The amt. of heat liberated in a muscle twitch is of the order of  $3 \times 10^{-3}$  cal. per g.; the amt. of energy associated with the elec. change in a muscle is negligible when compared with that liberated in the subsequent contraction. The amt. of heat produced in a nerve is of the order of  $3.5 \times 10^{-10}$  cal. or 0.015 erg per g. From the smallness of these quantities, no appreciable provision of energy is required in the propagation of the elec. response; and the physico-chem. change producing the response is the only factor involved in the propagated nervous impulse.

JOSEPH S. HEPBURN

**Physiology of cell division. VI. Excitation of cell division by wound hormones.** G. HABERLANDT. *Sitz. preuss. Akad. Wiss.* 1921, 221-34.—Exptl. evidence exists that the action of a wound as a stimulus in exciting cell division is due to decompn. products of the mechanically injured or dead cells. These products function as wound hormones. Cell division occurs not only when wound hormones pass from injured or dead cells into adjacent uninjured cells, but also frequently in the injured cells themselves if they survive and are adjacent to intact cells. Artificial parthenogenesis and the development of the fertilized ovum are likewise due to the formation and activity of wound hormones.

JOSEPH S. HEPBURN

**A study of the hemodynamic reactions of the cerebrospinal fluid and hypophyseal extracts.** CONRAD JACOBSON. Peter Bent Brigham Hosp., Boston. *Bull. Johns Hopkins Hosp.* 31, 185-97(1920).—A comparison was made of the physiological effects of intravenous injections of spinal fluid and hypophyseal exts. to det. the presence or absence of pituitary secretion in cerebrospinal fluid. The reactions obtained with concd. cerebrospinal fluid were identical with those following injection of various tissue exts. and no evidence was obtained indicating that the pituitary gland gives its secretion into the ventricles or into the cerebrospinal fluid. The pituitary gland exts. showed marked variability but all exerted a depressor effect common to the tissue ext. In general ext. of the anterior lobe exhibited a depressor effect mainly, posterior lobe ext. a moderate depressor followed by a pressor effect, and pars intermedia ext. a small depressor followed by a pressor effect. The whole gland showed a neutralization of the depressor and pressor effects. The posterior lobe ext. had an antidiuretic effect and produced glucosuria in a number of cases (more frequently in rabbits than in dogs). The depressor effect of cerebrospinal fluid is probably due to the depressor substance, histamine, found in all animal tissues and secretions, and not to any sp. secretion of the pituitary gland as was formerly contended.

A. P. LOTHROP

**The conditions under which the ratio between the urea content of the urine and of the blood remains constant.** T. ADDIS AND D. R. DRURY. Stanford Univ. Med. Sch. *Proc. Soc. Exptl. Biol. Med.* 18, 38(1920).—After administration of urea and H<sub>2</sub>O, the ratio between the urea in urine and in blood shows at first a variability; after the maximum urea concn. in the blood has been attained and the concn. is falling, the ratio becomes fairly constant for each individual. Food and excitement and other factors produce marked variations even under these conditions.

V. C. MYERS

**The effect of section of the nerves upon the water and salt secretion by the kidney.** PHILIPP ELLINGER. *Arch. exp. Path. Pharm.* 90, 77-104(1921).—Measurements of the secretory activity of the kidneys were made in dogs before and after the section of the major splanchnic, the vagus, and the renal nerves. The renal nerves exert a direct or an indirect inhibiting force upon the secretion of water and solids by the kidney. Section of the nerve to one kidney caused polyuria, with a decrease in the percentage



elimination of the solids and in the acidity, although there was an actual increase in elimination. The extent in reaction change may be so great that although the normal kidney continues to excrete an acid urine, that from the other kidney may be alk. to litmus. Apparently this change is not associated with the degree of polyuria. The secretion of chlorides was more strongly changed than any other factor. Section of the splanchnic also caused polyuria although of a less degree than section of the renal nerve. Solids, acidity, and N are decreased in percentage, but increased in actual amt., but not to the extent secured with renal nerve section. Chlorides are increased both in per cent and in actual amt., but not to a marked degree. Simultaneous section of the splanchnic and vagus increased the urine flow as much as 100-fold. The percentages of chlorides, acid, and N were essentially unchanged, thus there was a marked actual increase in amt. eliminated. The vagus alone appeared to exert an effect parallel to that of the splanchnic with respect to water elimination, but absolutely opposed to the splanchnic as regards secretion of solids. Apparently chlorides follow an individual law, as among the solid components of the urine, in the conditions governing secretion.

G. H. S.

**Respiration under very high pressure.** GUSTAV GAERTNER. *Arch. ges. Physiol.* 180, 90-5 (1920).—Mice were subjected to increased pressures of  $O_2$ , N and H. Pressures of 25 atm. were without lethal effect, regardless of whether the compression took place quickly or slowly. The duration of the compression, within certain limits, also was unimportant. The speed of decompression, however, had a marked effect, and detd. whether the animals lived or died. Apparently decompression without death could take place more quickly if the gas mixture was  $O_2$  and H, instead of N. It is suggested that helium be used, since it is non-combustible and is less diffusible than H. G. H. S.

**The blood of domestic animals examined by newer methods. II. Rabbit, hen, and pigeon bloods.** G. FRITSCH. *Arch. ges. Physiol.* 181, 78-105 (1920).—The detns. were made upon 10 individuals of each species; in each group 5 animals being males, 5 females. The erythrocyte count in rabbits av. 5.86 million. As in the case of the dog, horse and cow this value is somewhat higher than in man. The hemoglobin content of rabbit blood was relatively constant, with an av. value of 11.9 g. per 100 cc. of blood. The erythrocyte hemoglobin was  $20 \times 10^{-12}$  g. Leucocyte counts av. 8,900. Differential counts showed; lymphocytes 63%, mononuclear and transitional cells 1%, pseudocoinophils 31%, eosinophils 2%, basophils 2%. The thrombocyte number was high. The protein content of the plasma was 6.6%, detd. by refraction, the exponent being 1.3473. In the case of the hen the values depended upon sex. This is the only instance among domestic animals of any considerable difference in blood characteristics being referable to sex. In this species the erythrocytes were: male 3.24, female 2.77 million. Hemoglobin: male 12.3, female 9.6. The erythrocyte hemoglobin values were high, for the male 38, for the female  $35 \times 10^{-12}$ . Differential counts: lymphocytes, in the male 40%, female 64%; monos and transitionals, male 2%, female 5%; pseudocoinophils, male 49%, female 23%; eosinophils, male and females alike, 5%; basophils, males 3%, females 2%. Thrombocytes were few. The plasma protein was 6% in the males, 6.2% in the females. In pigeons the red cells were 3.18 million; hemoglobin was 13.7; erythrocyte hemoglobin number was  $43 \times 10^{-12}$ . The differential count showed 58% of lymphocytes, 3% of mononuclear cells, 35.5% of pseudocoinophils, 1.5% of eosinophils, 2% of basophils, and very few thrombocytes. The plasma protein of the pigeon, 4.3%, was the lowest value secured among the domestic animals. G. H. S.

**Spontaneous contraction of the surviving artery. I.** HELENE FRIEDMANN. *Arch. ges. Physiol.* 181, 206-12 (1920).—Strips of horse carotid artery were suspended in a const. temp. bath of Ringer soln. and stretched by attaching a load of 80 g. Immediately after the stretching a current of  $O_2$  was introduced to the bath and in some of



the expts. adrenaline also was added. Various atypical reaction responses were noted but as a rule the reaction was one of three types: (a) rhythmic contraction occurring suddenly within from 1 to several hrs. after the addition of the adrenaline, without a synchronous tonic contraction; (b) rhythmic activity and tonic contraction taking place simultaneously; or (c) rhythmic contraction being slowly superseded by tonic contraction. The freshness of the tissue was in a measure responsible for the type of reaction. The effect of sugar upon the contraction of arterial strips was detd. under similar conditions, and comparative expts. showed that the reaction capacity to adrenaline was significantly increased in sugar-contg. solns. This effect is not due entirely to the presence of sugar however, for further analysis of the reaction showed that the tonic contraction only was increased by the glucose, the rhythmic contraction being actually inhibited. Fructose and mannose exerted an effect comparable to that shown by glucose; arabinose, xylose, galactose, sucrose, and maltose were without effect. II. S. WEISS. *Ibid* 213-28.—Strips from the carotid artery of the ox were suspended in a bath of Ringer soln. and placed under tension with a wt. of 60 g. The length of the strips increased 2 or 3 fold. This excessive lengthening is compared with the  $1\frac{1}{2}$  fold lengthening of horse carotid under the same tension; the difference being ascribed to species variation. When the load was removed a tonic contraction, amounting to a shortening of about  $\frac{1}{3}$ , resulted. The size of the load and the resultant stretching modified the spontaneous contraction that followed removal of the wts. With a smaller load contraction occurred later; with a larger load, earlier. The presence of  $O_2$  was essential for the appearance of the spontaneous contraction. The addition of adrenaline induced a contraction which lasted about 9 min., and the tonic or rhythmic contractions, which normally began much later, were hastened in their appearance although the presence of adrenaline was not essential to their manifestation. The addition of glucose intensified the tonic but diminished the rhythmic contraction. Sucrose was without effect. The passage of  $CO_2$  through the bath caused a relaxation of the artery, with inactivity. Lactic acid acted much as  $CO_2$ . Choline in moderate dosage was inert, but was active in higher concns. Cocaine and atropine caused a prompt and protracted contraction. No evidence presented can be construed to indicate a neurogenic origin of the spontaneous contraction.

G. H. S.

The swelling of the cortex and of the arbor bundles of the cerebrum as a function of their chemical composition. A. WEIL. *Arch. ges. Physiol.* 179, 21-49 (1920).—Portions of nervous tissue were dried under various conditions and after drying the amt. of distd. water they would take up was detd. The amt. of water absorbed, expressed as % of the original water content, was greatest when the tissues were dried at  $60^\circ$  in *vacuo*. Temps. above and below this, with air-drying, gave lower values. Under the optimum conditions gray matter absorbed 99%, white matter 97%, and fetal brain (about 6 mos.) 98% of the original water content. By means of fractional extn. various factors were removed from the tissue and after each extn. the absorption capacity was detd. Gray matter dried at  $60^\circ$  in *vacuo* is given a % of 100 before extn., white matter in the same condition, a value of 96%. After water extn., involving the removal of sol. inorg. compds. and metabolic products, the percentages were: gray 100, white 99. Further extn. with acetone (removal of cholesterol, esters and phosphatides) gave values, for gray matter as well as for white, of 96%. Petroleum-ether extn. following the previous extns. removed the unsatd. phosphatides, and the tissues then gave: gray 81%, white matter 75%. An additional extn. with benzene (removal of cerebrosides, and P- and S-containing galactosides) gave 66% for the gray, and 94% for the white matter. A final extn. with alc. (removal of cerebrosides and satd. phosphatides) left the tissues in a condition where the gray matter absorbed 67%, the white matter 81%. Tables and graphs are presented indicating the detailed chem. changes



associated with these extn. procedures. A significant point is the increased absorptive capacity of the tissue after the water extn., indicating that the substances extd.→inorg. salts, metabolic end-products, and reserve materials of the cells—exert an inhibitory effect upon swelling. A further point of interest is the increase in swelling of the white matter following removal of the cerebrosides by benzene extn. Expts. were conducted to show the effect of temp. upon the swelling; both above and below body temp. a greater degree of swelling occurred. This two-fold reaction must be ascribed to substances other than the proteins or lipoids. Proteins appear to have a greater effect upon swelling than do the lipoids, and apparently it is the various combinations—lipoid-protein, lipoid-inorg. compd.—that exert the greatest influence. The swelling capacity of the cortex is greater than that of the nerve bundles.

G. H. S.

**The physiology of the thyroid. IX.** G. MANSFIELD. *Arch. ges. Physiol.* 181, 249-70(1920).—The paper is chiefly concerned with reaffirming certain earlier statements of the author and in justifying some of his conclusions which have been questioned by Hári. The particular points which are restated are: the increase in nitrogenous metabolism following an O<sub>2</sub> deficiency is associated with an increased thyroid activity; the administration of chloroform to normal animals increases nitrogenous metabolism but in thyroidectomized animals no such increase is noted; the fever induced by the injection of *B. coli* filtrates is not followed by increased nitrogenous metabolism in thyroidectomized animals.

G. H. S.

**The comparative physiology of digestion. VIII. Relation of yeast cells to proteases.** HEINRICH WALTER. *Arch. ges. Physiol.* 181, 271-84(1920).—Yeast was subjected to peptic and tryptic digestion processes and chem. and microscopical detns. were made to show the extent of the changes taking place. The chem. detns. correlated well with the changes observed microscopically. Previous extn. of the yeast with alc., ether, or chloroform did not greatly modify the results of the digestion. Yeast fat is in part diffused throughout the plasma and in part deposited in the fat bodies. After tryptic digestion these fat bodies can be readily extd., whereas before digestion extn. is difficult or impossible. There is always a portion of the plasma which is not digested, and which, by its indifferent reactions toward stains, does not appear to be a true protein. Of all vegetable foodstuffs yeast offers the most satisfactory substitute for meat.

G. H. S.

**Fibrin formation as a crystallization process.** HANS STÜBEL. *Arch. ges. Physiol.* 181, 285-309(1920).—The processes of fibrin formation were studied by ultramicroscopic methods. Several animal species were investigated. In Crustacea, whose blood clots firmly, ultramicroscopic examn. shows the formation either of a diffuse granular ppt., or the development of isolated weakly refractile filaments. In other crustacean forms, where the clot structure is less firm, both the granular and filamentous processes take place. The granules have a tendency to unite in series to form fibers, so that there are many forms transitional between true granules and well formed fibers. Reactions of this type occur in the Mollusca and in insects. In vertebrates, except the Mammalia, the coagulation process is associated with the formation of a rather tough, dense network of fibers; rarely are isolated needle-shaped structures to be seen. In mammals the process of coagulation proceeds as a typical crystn. process, the fibrin deposition consisting of a dense network of individual needles. These structures may increase in size during the process of crystn. All of these types of fibrin deposition,—as granules, fibers, or needles,—are essentially of the same physico-chem. nature; a crystn. process.

G. H. S.

**A direct proof of the impermeability of human and rabbit blood corpuscles to glucose.** S. VAN CREVELD AND R. BRINKMAN. *Verslag Akad. Wetenschappen Amsterdam* 29, 863-8(1920).—Any direct chem. test of permeability of blood corpuscles



to glucose should use only plasma taken direct from the blood vessels or prepd. from fresh blood which has not begun to coagulate and has not been treated to prevent coagulation. This can be done, for rabbits, by removing about 2.5 cm. of the jugular vein, tying it at each end, and sepg. the corpuscles by gravity or by centrifuging. For human blood, attempts to utilize fresh navel cords and placenta were only partially successful. Satisfactory sepn., without any coagulation, is possible by centrifuging fresh blood quickly in small paraffined tubes. From the total sugar content and that of the plasma, and the relative vol. of corpuscles and plasma, the sugar content of the corpuscles was calcd. and found to be practically nil. This is considered to be sufficient proof that the blood corpuscles of rabbit and man are impermeable to glucose. The opposite opinion, expressed by various investigators, is attributed to the use of samples in which incipient coagulation has set in. Hirudin and other anti-coagulants do not prevent the first stages of coagulation. Moreover, detns. made by adding glucose to the blood are not reliable because the permeabilities to  $\alpha$ - and  $\beta$ -D-glucose may be different. Another factor is the possible formation of a glucose colloid compd. JULIAN F. SMITH

The relation of calcium-ion concentration to the stomach movements induced by irritation of the vagus nerve. R. BRINKMAN AND (Miss) E. VAN DAM. *Verslag Akad. Wetenschappen Amsterdam* 29, 899-907(1920).—The sensitivity of a vagus nerve, numbed by a current of 0.6% NaCl ( $p_H = 8.6$ ), is rapidly restored by a current of a soln. of NaCl (0.5%),  $\text{NaHCO}_3$  (0.28%),  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (0.040%) and KCl (0.020%) ( $p_H = 8.6$ ). Addition of 0.015%  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to a soln. of 0.6% NaCl + 0.02% KCl prevents any decrease in sensitivity of the vagus nerve, provided the  $p_H$  is kept const. at 8.6. Rubber tubing should not be used, since it is likely to increase the acidity.  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  at concns. of 0.02% or higher will not protect the sensitivity. Addition of 0.28%  $\text{NaHCO}_3$  to the soln. as a buffer, permits the  $p_H$  to go as low as 7.7; at 7.3 the sensitivity decreases noticeably, and at 7.1 it practically disappears. Lower concns. of  $\text{NaHCO}_3$  are not sufficient. It is uncertain whether the effect is due to a direct influence of  $\text{HCO}_3^-$  or only to its influence on the  $\text{Ca}^{++}$  concn. Evidence favors the latter view. JULIAN F. SMITH

#### G—PATHOLOGY

H. GIDEON WELLS

Studies on the nature of the action of non-specific protein in disease processes.

II. Horse serum and soluble toxin. D. M. COWIE AND R. M. GREENTHAL. Univ. Mich. *J. Med. Research* 42, 261-8(1921).—One cc. of normal horse serum injected subcutaneously or intravenously into guinea pigs simultaneously with diphtheria toxin will always protect against a fatal dose and may protect against as high as 8 fatal doses of the toxin. Larger doses of normal horse serum protect against larger doses of diphtheria toxin but the effect is not necessarily proportional. The protecting power of normal horse serum resides in the protein portion and not in the alc.-sol. portion. The protein portion of 1 cc. of horse serum always protects against a fatal dose of toxin. There seems to be evidence that the protecting power of the horse serum used was not entirely due to the presence of diphtheria antitoxin in the serum. E. B. FINK

The precipitins in blood sera of arthropods. LEO LOEB. St. Louis. *J. Med. Research* 42, 269-75(1921).—*Limulus* serum, mixed with those heterologous sera of arthropods which have so far been tested, produces a ppt. provided the proportions are suitable. It is probable that a constituent of the unheated *Limulus* serum plays the part of a precipitin and a constituent of the heterologous serum that of a precipitable substance and that both chem. and physical factors underlie the pptn. E. B. FINK

The specific adaptation between body fluids and blood cells in invertebrates. LEO LOEB. St. Louis. *J. Med. Research* 42, 277-88(1921).—There is a sp. adaptation between the blood cells of *Limulus* and *Limulus* serum. In *Limulus* serum the out-



growth of the exptl. cell fibrin tissue is better than in any other kind of serum so far tested. It is probable that in general only a species (hetero) reaction exists in invertebrates and that the individuality (homoio) reaction becomes universal first in the lower vertebrates.

**The pigmentation of heart muscle.** DAVID H. DOLLEY AND FRANCES V. GUTHRIE. Univ. Mo. *J. Med. Research* 42, 289-301 (1921).—An exogenous pigment derived from the plant carotinoids and carried in the blood plasma may appear in heart muscle. It is an adventitious pigment and may occur under normal conditions and be exaggerated in disease. It is a lipochrome. An endogenous pigment derived from disturbed metabolic processes is the pigment proper of brown atrophy of the heart. It is melanin. There appear to be just 3 groups of pigments involved in body metabolism: the lipochrome of exogenous origin, and the melanins and blood pigments of endogenous origin. The formation of melanin by cells, which normally do not produce it, must be admitted as a result of the abnormal metabolism of depression.

E. B. FINK

**The pellagra outbreak in Egypt. I. Pellagra among Ottoman prisoners of war.** A. DOUGLAS BIGLAND. *Lancet* 1920, I, 947-53.—From the exptl. side all efforts to obtain organisms from the blood and feces on various media, complement fixation with alc. exts. of organs obtained at autopsy, inoculation of rabbits with pellagrous sera and the diagnostic use of maize exts., failed of positive results. An examn. of the diets of these pellagrins showed that there was a deficiency in the "biological value of protein," but there were a few cases in which no such deficiency could be proved. To explain these cases, it is assumed that some toxin is formed which acts upon the intestine or its contents in such a way that protein is not properly assimilated.

E. B. FINK

**The Schick reaction and diphtheria prophylactic immunization with toxin-anti-toxin mixture.** A. T. GLENNY, K. ALLEN AND R. A. O'BRIEN. London. *Lancet* 1921, I, 1236-7.—A brief review.

E. B. F.

**Hippuric acid synthesis tests as regards the functional condition of the kidney.** P. L. VIOLETTE. *Vittel. Lancet* 1921, I, 1239; cf. *C. A.* 15, 1926.—In the cases under observation it was found that the renal condition, as evidenced by the hippuric acid synthesis test, is fairly closely related to arterial hypertension. Azotemia, chloridemia and albuminuria are evolved in crises. The modifications observed in the hippuric acid synthesis appear to be reflections of functional parenchymatous disturbances that are capable of gradual modification. Hepatic disturbances when not accompanied by renal disturbances fail to effect any modifications in the hippuric acid synthesis, which appears to be of purely renal origin. From the point of view of hydrology these findings may explain the results obtained in cases of arterial hypertension by means of treatments by diuretic waters which act energetically on the kidney parenchyma.

E. B. FINK

**Fat content of the blood and the fat and glycogen content of the liver in diabetic coma.** H. C. GRØNLMYNDEN. *Acta Med. Scand.* 53, 381 (1920); *Physiol. Abstracts* 5, 558; cf. *C. A.* 14, 2513.—The percentage of glycogen in diabetic livers varied from 0.06 to 3.03; fat from 2.63 to 7.32. In non-diabetic cases the liver glycogen was from 0.06 to 0.20. There is no simple relation between liver glycogen and liver fat. The differences found between acute exptl. diabetes and that taking place in man are due to the difference in the velocity with which sugar is formed from fat in the body. In ablation of the pancreas the pancreatic hormone is removed more rapidly and completely than in human diabetes.

H. G.

**The presence and importance of coagulins in immune sera.** C. SARTI. *Ann. igiene* 29, No. 6; 349-58 (1919); *Expt. Sta. Record* 43, 581.—This is a report of a study of the phenomenon of coagglutinin formation in dogs immunized against various organisms. In the course of immunization against typhoid and paratyphoid A and B of



normal dogs, the sera of which originally contained no agglutinins against the various organisms used, not only were agglutinins formed for the sp. organisms, but the sera acquired agglutinating power against organisms of a different species from that serving as antigen. Weak agglutinating power for the sp. organism corresponded with weak secondary agglutinating properties, which became stronger with stronger sp. agglutinating power. The strength of the secondary agglutinins was not, however, in strict proportion to that of the primary, and differed with the various antigens employed. Both the primary and secondary agglutinins in dogs were located principally but not exclusively in the pseudoglobulin fraction of the serum. H. G.

**Researches on agglutination. Continued action of an electric current on agglutinating sera.** P. ZANNELLI. *Ann. igiene* 30, 405-7(1920); *Expt. Sta. Record* 43, 781-2.—To study the action of the elec. current on agglutinating sera, typhoid, paratyphoid A, paratyphoid B, and cholera agglutinating sera were exposed in U tubes to an elec. current of 8 v. and 0.0005 amp. for a period of 2 hrs. At the end of this time that portion of the serum in the branch of the tube corresponding to the cathode was turbid with a strongly alk. reaction, while that in the other side appeared gelatinous and gave an acid reaction. Tested separately both portions of the serum reacted negatively to agglutination tests, but when brought together again exhibited the original agglutinating power. Z. is of the opinion that the action of the elec. current causes the division of the agglutinins into two parts, each of which has no agglutinating power. H. G.

**Pathogenesis and metabolism processes in diabetes insipidus with special consideration of the chemical investigation of the blood.** H. GÖRKE. *Arch. Verdauungskrankh.* 26, 364-98(1920); *Physiol. Abstracts* 5, 564.—G. agrees that there is a relation between the hypophysis and diabetes insipidus; subcutaneous or intravenous injections of pituitary exts. remedy the condition temporarily. The blood exhibits hyperchloremia and hyperosmosis, but absence of NaCl in the food does not produce a normal state of things. H. G.

**Studies of blood enzymes in pregnancy carcinoma or pulmonary tuberculosis.** J. GRÖNBERG. *Finska. Lak. Handlingar.* 62, 599-631(1920); *Physiol. Abstracts* 6, 93.—The Abderhalden reaction gave only positive results for 28 cases of pregnancy, 23 of carcinoma, and 34 of pulmonary tuberculosis when proper precautions were taken. H. G.

**The complement-fixation reaction in tuberculosis.** W. W. WATKINS AND C. N. BOYNTON. *J. Am. Med. Assoc.* 75, 933-7(1920); *Expt. Sta. Record* 44, 279.—This is a statistical report of results obtained in 6,500 complement-fixation reactions for tuberculosis, together with a discussion concerning the relative value of different antigens, the specificity of the reaction, and the clinical value of the results. The authors are of the opinion that there is little to influence a choice of antigens provided the whole bacillus is used and thoroughly broken up. They consider the reaction to be sp. for tuberculosis, a positive reaction indicating active or recently active tuberculosis, and a negative reaction either absence of infection, excessive activity of the disease exhausting the antibody, or arrest of the disease with spontaneous disappearance of antibody no longer required. H. G.

**Pellagra.** A. VISWALINGAM. *J. Trop. Med. Hyg.* [London] 21, No. 15, 153-8 (1918); *Expt. Sta. Record* 43, 263.—Various theories regarding the cause of pellagra are reviewed briefly, and applied to the etiology of the disease as found among the Chinese field laborers in the Malay States. A summary is given of the symptomatology, diagnosis, prognosis, and treatment of the disease, and several case reports are included. H. G.

**Some further observations on the etiology of "pellagra."** A. VISWALINGAM



*J. Trop. Med. Hyg.* [London] **23**, No. 4, 46, 47(1920); *Expt. Sta. Record* **43**, 263-4.—Further evidence is given in confirmation of the view (cf. preceding abstract) that both the deficiency and the parasite theory hold good in the etiology of the disease among the Chinese in the Malay States. The freedom of the Malay and Tamil laborers from the disease is thought to be due chiefly to the better quality of their diet, which includes a variety of fresh vegetables and more or less meat. That faulty diet is not solely responsible for the disease is shown by the seasonal recurrences of symptoms in patients placed in a hospital with adequate diets for considerable periods of time. "Whether the infecting agent is an organism which enters the gastro-intestinal system and produces a toxin which gets absorbed into the system and produces the varied symptomatology, or whether owing to a deficiency in the vitamins some deleterious products are created in the intestines and give rise to an intoxication of the system, it is difficult to say at present." H. G.

Action of hypophysis extract on the excretion of water in diabetes mellitus. ANON. *Med. Klinik* (Vienna) **16**, 569-70(1920); *Physiol. Abstracts* **5**, 564.—Pituitary ext. had no effect in reducing the amt. of urine. The diuretic effect of sugar is too strong for any opposite effect which the ext. may have to overcome it. H. G.

Black colostrum. JOHAGERMANN. *Med. Klinik* (Vienna) **16**, 902(1920); *Physiol. Abstracts* **5**, 597.—The case is described of a woman who secreted from both breasts a colostrum of black-green color. The secretion was sterile, and melanin, alcapton, blood, drug action, malignancy, and other factors were excluded. The colostrum corpuscles were loaded with the pigment. Its possible origin is discussed, but with no conclusion. H. G.

New contribution to the knowledge of inorganic substances of the blood. I. Cations and hyperphosphatemia in Bright's disease. J. FEIGL. *Z. physiol. Chem.* **111**, 280-6(1920); *Physiol. Abstracts* **6**, 39.—The "acid-soluble" P content of the blood is much higher than normal, while the K, Na, Ca, and Mg do not increase to anything like the same extent. On the other hand, the NH<sub>4</sub> rises to as much as 8 times the normal amt. H. G.

The carbon dioxide absorption curve and carbon dioxide tension of the blood in cardiac dyspnea. JOHN P. PETERS, JR. AND DAVID P. BARR. Russell Sage Inst. and Bellevue Hosp., N. Y. *J. Biol. Chem.* **45**, 537-70(1921); *C. A.* **15**, 1749.—CO<sub>2</sub> absorption curves were detd. for the bloods of 7 patients with cardiac decompensation and dyspnea but without signs of renal involvement. Three of these curves were below the normal range. Compensation was later established in 2 patients and the curves became normal. However, no relation could be established between the reduction in the level of the curve and the severity of the symptoms or the degree of unsatn. of the arterial or venous blood. The reduction in alk. reserve indicated by the low level of the curve is not reflected in the CO<sub>2</sub> capacity of the plasma as this is ordinarily determined because the plasma is separated from the cells at the CO<sub>2</sub> tension existing in the circulating blood and, in these cases, this was above the normal. It is suggested that either whole blood be used for the detn. of the CO<sub>2</sub> capacity or else that the blood be equilibrated with a standard air-CO<sub>2</sub> mixt. before centrifuging. In 4 cases, alveolar, arterial and venous CO<sub>2</sub> tensions were detd. or calcd. Though the difference between arterial and venous CO<sub>2</sub> content or tension was sometimes greater than normal no consistent increase was observed. In 2 cases there was a definite CO<sub>2</sub> retention with consequent increase of H-ion concn. The difference between alveolar and arterial CO<sub>2</sub> tension was increased from 13 to 19 mm. The significance of these observations is discussed and it is suggested that the primary disturbance is in the impairment of the efficiency of the pulmonary mechanism for the exchange of gases between the blood and the outside air. I. GREENWALD



The carbon dioxide absorption curve and carbon dioxide tension of the blood in severe anemia. DAVID P. BARR AND JOHN P. PETERS, JR. Russell Sage Inst. and Bellevue Hosp., N. Y. *J. Biol. Chem.* 45, 571-92(1921).—A study of the  $\text{CO}_2$  absorption curves of the bloods of 6 patients with severe anemia (3 pernicious, 1 probably pernicious and 2 gastric carcinoma). The curves are flatter than normal, owing to, but not proportional to, the diminution in hemoglobin. The arterial H-ion concn. was calcd. in 3 cases and found to be low, as low as  $10^{-7.47}$  in 1 case; the venous H-ion concn. in 4 cases varied between  $10^{-7.32}$  and  $10^{-7.43}$ . The abnormally great differences in H-ion concn. of arterial and venous blood are due to the decrease in the  $\text{CO}_2$ -carrying capacity of the blood and to the decrease in the compensating effect of  $\text{O}_2$  unsatn. These differences may explain the dyspnea of anemia. Cf. preceding abstr. and C. A. 15, 1749. I. GREENWALD

Iodine in the treatment of goiter. S. P. BEEBE. *Med. Record* 99, 996-9(1921).—Iodine as KI, FeI, and in thyroid ext. answer all the requirements for therapeutic purposes in cases of thyroid disorder. F. S. HAMMETT

Heat production in diabetes mellitus. W. ARNOLOI AND E. KRATTER. *Z. expil. Pathol. Therap.* 22, 92-107(1921).—The oxidation processes of the diabetic and non-diabetic are not considered essentially different in principle. F. S. HAMMETT

Does a negative Schick test indicate present and future security from diphtheria? WILLIAM H. PARK. *Arch. Pediatrics* 38, 329-35(1921). Diphtheria prevention work in the public schools of New York City. ABRAHAM ZINGHER. *Ibid* 338-59. The Schick test in private practice. DEVER S. BYARD. *Ibid* 360-4. Preparation of mixture of diphtheria toxin-antitoxin. EDWIN J. BANCRAF AND CHARLES K. GREENWALD. *Ibid* 365-7. The duration of the immunity conferred by the use of diphtheria toxin-antitoxin. M. C. SCHROEDER. *Ibid* 368-72.—These addresses form a symposium on modern methods for prevention of diphtheria before the New York Academy of Medicine, May 23, 1921. JOSEPH S. HEPBURN

Origin of salivary calculus. HERMANN PRINZ. Univ. Penn. *Dental Cosmos* 63, 369-74, 503-10, 619-24(1921); cf. C. A. 15, 1352.—The exhaustive review of the literature is completed; and results of original work are reported. Teeth were imbedded in modeling compd., narrow spaces being left on both the buccal and lingual sides beneath the gingival margin to simulate the pyorrhea pockets. They were then kept at a temp. of  $40^\circ$ ; and the pockets were filled daily with fresh saliva. At the end of 8 to 10 weeks, the teeth were removed from the compd.; they presented typical tartar incrustations upon their roots, identical in every respect with the salivary calculi occurring upon teeth in the human mouth. The same result was obtained when this expt. was repeated, a synthetic saliva, prepd. from dried albumin,  $\text{CO}_2$ , and inorg. salts ( $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{PO}_4$ ,  $\text{Na}_2\text{PO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Mg}_3(\text{PO}_4)_2$ ), being substituted for fresh saliva. When a test tube was filled with fresh saliva and permitted to stand, a pellicle formed at the surface of the saliva within approx. 1 hr., and finally sank slowly to the bottom of the tube; additional pellicles then formed and took the same course; they were colloidal and contained Ca. A section is devoted to the prevention of the formation of tartar and to dentifrices. Ingestion of  $\text{NaHCO}_3$  (5 grains twice daily between meals) or of alk. waters is stated to decrease the tendency to form tartar, while acid foods and drinks increase the tendency. A bibliography is appended. JOSEPH S. HEPBURN

Comparison of mumps and chronic lead poisoning from the standpoint of the totality of the symptoms. CONRAD WESSELHOEFT. *J. Am. Inst. Homeopathy* 14, 13-29(1921).—The symptoms of chronic Pb poisoning and those of mumps resemble each other in many respects. The most striking similarity is the parotitis, commonly complicated by orchitis which is often followed by testicular atrophy. A bibliography of 67 references is appended. JOSEPH S. HEPBURN



**Studies on the transplantation of organs.** L. MÖLLER. *Réunion soc. belge biol.* 1920, 202; *Physiol. Abstracts* 5, 198(1920).—The technic of the transplantation of organs is complicated by the necessity of attaining a good vascular coaptation. On the other hand, metastases of malignant neoplasms grow with unpleasant ease. These facts suggest that normal tissues may be transplanted by distributing fragments of such tissues in the proper regions such as the peritoneum. The fragments must be sufficiently small to be able, for the time at least, to obtain nutrition by simple diffusion. This technic has been used with a certain degree of success in the study of the origin of vaccinal hemolysins. Fragments of the spleen, omentum, bone marrow and thyroid were obtained from immunized animals and introduced into the peritoneum of other animals, and imparted to the latter animals at least a portion of the immunity which they had acquired prior to transplantation. The thyroid gland was removed from one dog, coarsely divided, and introduced into the peritoneum of a second dog, upon which thyroidectomy was then performed 5 days later; organotherapy was omitted at the end of 1 week; the animal survived for several months and never showed any symptoms of thyroid insufficiency.

JOSEPH S. HEPBURN

**Pathogenesis of diabetes insipidus.** JULIUS BAUER AND BERTA ASCHNER. *Wiener Arch. inn. Med.* 1, 297-334(1920).—A description is given of a case of diabetes insipidus in which the vol. of urine was markedly decreased after the administration of pituitrin infundibular. The role that the secretion of the hypophysis may play in influencing the vol. of urine is considered as well as other possible causes of diabetes insipidus.

HARRIET F. HOLMES

**Further observations on Bence-Jones albuminuria in leucemia.** ALFRED DR-CASTELLO. Vienna. *Wiener Arch. inn. Med.* 1, 335-58(1920).—Including three cases in the author's own experience, eight cases of leucemia are collected in which the Bence-Jones body was found in the urine. In an additional case a strange protein was found which after dialysis and acidification of the urine gave the reactions of the Bence-Jones body. The Bence-Jones body was found in both lymphatic and myeloid leucemias. The amt. found was low as compared with the very large amts. reported in myeloma cases. In the lymphatic leucemias the amt. of the Bence-Jones body was not influenced by X-ray treatment, but X-ray treatment combined with benzene and arsphenamine has caused its disappearance from the urine. In myeloid leucemia the Bence-Jones body has disappeared under benzene treatment alone, and also under X-ray treatment, if the author's doubtful case be reckoned as a Bence-Jones albuminuria. This is in line with the behavior in general of lymphatic and myeloid leucemias towards treatment with X-ray and benzene.

HARRIET F. HOLMES

**The urochromogen fraction of the urine.** M. WEISS. Vienna. *Wiener Arch. inn. Med.* 1, 358-70(1920); cf. *C. A.* 15, 1141.—The urochromogen reaction in the urine as given by Ehrlich's diazo reaction or the author's permanganate reaction, is often obscured by the presence of substances such as urobilin or bilirubin. By treatment of the urine with  $(\text{NH}_4)_2\text{SO}_4$  and filtering, the filtrate contains only traces of urobilin or bilirubin. In cases giving a doubtful reaction a positive reaction can often be obtained by the following method: 500 cc. urine are treated with 40 g. Pb acetate and after it has stood a half hour 25 cc. of 10% "alkali" is added. The ppt. which contains the urochromogen and other coloring matter is treated with 25 g. "Na phosphate." A little water is added and the filtrate is made weakly acid; to 25 cc. of the liquid 20 g.  $(\text{NH}_4)_2\text{SO}_4$  is added. The filtrate from this is called the urochromogen fraction of the urine. This gives the diazo or the permanganate reaction with great intensity if positive. A quantitative detn. can be made by adding to the diluted urochromogen fraction a permanganate soln. of known strength until the diazo reaction disappears, or Ehrlich's diazo method may be used and the urochromogen fraction diluted until the color corresponds to the diazo reaction of a



1:3000 soln. of tyrosine in 1% soda solution. The diazo value is the amount of tyrosine that, dissolved in a quantity of fluid equal to the day's urine, would give a similar diazo reaction. In normal urines there is present urochrome, a normal product of metabolism, which is more highly oxidized than urochromogen and which does not give the characteristic diazo reaction. By using large amounts of urine a diazo value between 0.10-0.15 may be obtained. A diazo value above 0.16 in pathological urines giving a negative diazo reaction may be of clinical importance as indicating a probable tuberculous etiology.

HARRIET F. HOLMES

The distribution of cholesterol and its esters between blood corpuscles and plasma under physiological and pathological conditions. M. RICHTER-QUITTNER. Vienna. *Wiener Arch. inn. Med.* 1, 425-54(1920).—The total cholesterol is divided equally between plasma and blood corpuscles in normal conditions, in alimentary hypercholesterolemia and generally in pathologic hypercholesterolemia. Occasionally the cholesterol is higher in the plasma than in the corpuscles in pathologic hypercholesterolemia. The blood corpuscles of man and of all animals studied contain cholesterol only in the free form and are free from cholesterol esters under both physiologic and pathologic conditions. The administration of fat or food rich in cholesterol or free cholesterol causes an increase of cholesterol in the blood. This physiologic hypercholesterolemia affects both the free cholesterol and its esters. First there is an increase of cholesterol esters in the plasma, and then after some hours a part of the cholesterol esters enters the blood corpuscles. At the moment of entering the blood corpuscles saponification must take place as cholesterol esters are never found in the corpuscles. In pathologic hypercholesterolemias only the free cholesterol is increased, the cholesterol esters remaining normal in amount. In all normal cases the blood corpuscles contain only free cholesterol and the plasma only cholesterol esters. On the contrary in pathologic hypercholesterolemia in addition to small amounts of cholesterol esters, the plasma contains much free cholesterol. Administration of fat or food rich in cholesterol or free cholesterol causes an increase of the cholesterol esters in pathologic hypercholesterolemias as well as in physiologic hypercholesterolemias.

HARRIET F. HOLMES

Anaphylaxis. H. G. WELLS. Univ. Chicago. *Physiol. Reviews* 1, 44-83(1921); *Physiol. Abstracts* 6, 93(1921).—A critical review of the entire subject in which is emphasized the necessity of strict definition of the term anaphylaxis, and the sepn. from anaphylactoid phenomena. The chemical basis is emphasized and the problem of specificity discussed at length, with the conclusion that as yet specificity demonstrable by immunological methods corresponds to distinguishable chemical differences in the proteins. The author does not accept as conclusive the evidence so far presented that true anaphylaxis can be produced by anything except complete protein molecules, although he admits the possibility that non-protein substances may combine with body proteins to produce antigenic foreign proteins.

E. R. LONG

The influence of systemic changes on local tissue reactions. J. AUER. Rockefeller Inst. Med. Research. *Proc. Soc. Exptl. Biol. Med.* 17, 93-4(1920).—By comparison of control and sensitized rabbits on the basis of the production of edema after irritation of the skin with xylene, it appears that sensitized animals, which have circulating ineffective amts. of the antigen, may react locally with anaphylactic changes if through any mechanism (inflammation and edema) an effective dose of the antigen accumulates in these tissues.

V. C. MYERS

The carbon dioxide dissociation curve and the arterial and venous carbon dioxide tension of human blood in health and in disease. J. P. PETERS, JR. AND D. P. BARR. Russell Sage Inst. and Bellevue Hosp. *Proc. Soc. Exptl. Biol. Med.* 18, 6-9(1920).—The method consists in the simultaneous detn. of the CO<sub>2</sub> dissociation curve of blood at body temp. and the CO<sub>2</sub> content of arterial and of venous blood as they occur in



the body. In 3 out of 7 cases with cardiac decompensation the dissociation curve was found to be below normal, while in severe anemia it was higher than normal. An empirical equation to correct the  $\text{CO}_2$  tension of arterial and venous blood for  $\text{O}_2$  unsatn. is proposed.

V. C. MYERS

An attempt to produce hemochromatosis experimentally. L. R. CHANDLER. Stanford Univ. *Proc. Soc. Exptl. Biol. Med.* 18, 24-5(1920).—An attempt was made to test the theory that hemochromatosis may be due to Fe retention, from decreased excretion of waste Fe by the colon. The total removal of the large intestine in dogs apparently does not produce hemochromatosis within a period of  $3\frac{1}{2}$  months.

V. C. MYERS

Further observations on ether hyperglucemia in the absence of the adrenals. G. N. STEWART AND J. M. ROGOFF. *J. Pharm. Proc.* 15, 238-9(1920); cf. *C. A.* 14, 2369.—Confirmation of previous results that marked hyperglucemia is caused in rabbits which have survived the removal of both adrenals, by light narcosis and surgical anesthesia produced by the administration of  $\text{Et}_2\text{O}$  for 15 min. to 1.5 hrs. A further increase can be obtained by subjecting the animals to asphyxia begun about 15-20 min. after etherization was discontinued.

C. J. WEST

## H—PHARMACOLOGY

ALFRED N. RICHARDS

Theory of narcosis. KURT H. MEYER AND HANS GOTTLIEB BILLROTH. *Z. physiol. Chem.* 112, 55-79(1921); *Munch. med. Wochschr.* 68, 8-10(1921).—As a result of detns. of soln.-coeff. of 12 narcotics and their action on mice, the lipid theory of narcosis is supported. Narcosis results when the anesthetic reaches a definite molar concn. in the cell lipid. This critical concn. is in general independent of the properties of the narcotic but depends upon the kind of animal involved. Since substances of widely different chem. nature act similarly as narcotics this action must be physical and not chem. Changes in the cell lipid are produced by equimol. concn. of the anesthetic just as the b. p. is depressed to the same degree by equimol. proportions of different solutes.

H. V. ATKINSON

The comparative toxicity of thymol and carvacrol (isothymol). A. E. LIVINGSTON. *U. S. Public Health Reports* 36, 1317-31(1921); *J. Pharmacol.* 17, 261-75(1921).—L. has made a study of the comparative toxicity and anthelmintic value of carvacrol and thymol. Thymol has been used widely in this country as a remedy for uncinariasis, but, being of foreign manufacture, its supply is not assured. Since a method for the prepn. of carvacrol has been worked out in this country, its supply is certain and comparatively cheap. It is suggested that carvacrol be used as a substitute for thymol, since the former is physiologically as effective, of about an equal toxicity, and at the same time, being a liquid, is physically better adapted to its role of intestinal antiseptic than the solid and equally insol. thymol. Expts. made on rabbits and on *Paramecia* showed that the toxicity of thymol and carvacrol is essentially the same in each case. Tests on earth worms indicated that the relative anthelmintic value of thymol and carvacrol is practically the same.

J. A. BRADLEY

Flavine and its uses in veterinary practice. C. A. ZELL. *Am. J. Vet. Med.* 15, No. 4, 144-7(1920); *Expt. Sta. Record* 43, 79.—Z. reviews briefly the studies of Browning Gulbransen, et al. (*C. A.* 11, 2916) on the value of acriflavine and proflavine as antiseptics and reports the general results obtained in lab. and field expts. in the application of these antiseptics to veterinary practice. As proflavine in the lab. tests proved to have stronger bactericidal powers for some of the common pathogenic organisms and acriflavine for others, a prepn. contg. both dyes was used in the field tests. Excellent results are reported with flavine treatment in a number of cases of suppurating wounds



fistulas, hemorrhagic septicemia, purpura hemorrhagica and pleural pneumonia. In the case of wounds, abscesses etc., the affected places are packed with gauze satd. with the flavine soln. In cases of septicemia and other diseases of infectious origin, the antiseptic is injected intravenously in 1:1,000 diln. in normal salt soln. H. G.

**Study of hypophysis.** A. SILVA. *Inaug. Dissert.*, Santiago, 1917; *Physiol. Abstracts* 6, 72.—In normal subjects pituitary exts. give rise to vascular hypotension. In the tachycardia of Graves' disease they produce also polyuria, transient glucosuria, pallor of the skin, and contractions of the intestines and uterus. H. G.

**Hemolysis through oligodynamic metal action.** L. HESS AND R. REITLER. *Med. Klinik* 16, 976-8(1920); *Physiol. Abstracts* 5, 573-4.—NaCl solns., which were in contact with metals, have hemolytic effects. The degree of the hemolysis depends on the metal (Cu>Cd>Pb>Ag>Ni>Mo>Sb>Sn>Al), on the diln. of the blood corpuscles (with higher dilns. a better hemolysis), on the temp., and on the duration of the contact between the metal and the soln. The hemolysis is inhibited when serum is used instead of the salt soln. H. G.

**The effect of cyanide and of organic oxidizing agents on the liver injury caused by chloroform.** N. C. DAVIS. Univ. Calif. Med. School. *Arch. Intern. Med.* 28, 20-36(1921).—"Very small amts of CHCl<sub>3</sub> given subcutaneously are sufficient to cause an extensive liver injury in fasting animals. The intravenous injection of small amts. (up to 60 mg. per kg.) of organic oxidizing agents (iodoxy and iodo-benzoic acids and their Na salts) seems to have no effect on CHCl<sub>3</sub> liver necrosis. Larger amts. of these substances given subcutaneously appear to afford the liver some protection against CHCl<sub>3</sub> injury. The administration of cyanides (K and Na) does not affect CHCl<sub>3</sub> liver injury in any constant manner; it seems that larger doses may exert some protective action. These expts. offer no evidence that CHCl<sub>3</sub> liver injury is a result of disturbance in tissue oxidations." I. GREENWALD

**Quinine hemolysis.** ALFRED LUGER. *Biochem. Z.* 117, 145-52(1921).—L. reports the results of his study of the action of quinine in various concns. on blood corpuscles in various concns. of hypotonic NaCl, in the presence of saponin, various acid and alk. salts, urea and immune amboceptors. The results of Rusznyak (cf. C. A. 15, 384) for acid and alk. hemolysis were confirmed. The acceleration of hemolysis by quinine in the presence of NaCl solns. is considered important. When red corpuscles have been previously treated with quinine they show in the presence of NaCl a decreased resistance to H<sub>2</sub>O and immune hemolysin, and increased resistance to saponin, and no change in alcohol hemolysis. These findings do not agree with those of Rusznyak. F. S. HAMMETT

**The behavior of phrenosin in the animal body.** TOMIHIDE SHIMIZU. *Biochem. Z.* 117, 263-5(1921).—A dog was fed with 3 g. of phrenosin for 5 days. The urine was collected and examd. for split products of the administered compd. The reaction of the urine was acid; the Hopkins-Cole test was strongly positive; the Uffelmann reaction was negative and no sugar was present. Sphingosine could be isolated from the urine. After feeding to or injecting sphingosine into a dog or rabbit the same can be recovered from the urine. No disturbances of the nervous system were noted. F. S. HAMMETT

**The behavior of pyrrole in the animal body.** I. TOMIHIDE SHIMIZU. *Biochem. Z.* 117, 266-8(1921).—S. injected daily for 6 days 0.6 g. of pyrrole into an 11-kg. dog, and 0.3 g. for 7 days into a 3.5-kg. rabbit. Throughout there was no blood, protein or bile-pigment excretion. Methylpyridine was recovered from these urines. F. S. HAMMETT

**The influence of pilocarpine on the composition of the blood.** A. BORNSTEIN AND ROBERT VOGEL. *Biochem. Z.* 118, 1-14(1921).—When pilocarpine is administered



to dogs it causes a noticeable decrease in the  $H_2O$  content of the blood. This is accompanied by an increase in the relative hemoglobin content, an increase in the number of red corpuscles and an increase in the protein content. These changes are attributed to a basic displacement of the  $H_2O$  distribution of the body, in which a loss of  $H_2O$  by excretion, secretion and increased insensible perspiration plays but a small part. Pilocarpine produces in both dogs and rabbits a hyperglucemia. None of these effects of pilocarpine are affected by extirpation of the spleen. Atropine exerts an antagonistic action towards all the phenomena brought about by the former drug. F. S. HAMMETT

The fate of parenterally administered sulfur and its influence on metabolism. ROBERT MAYER-BISCH AND E. BASCH. *Biochem. Z.* 118, 39-49(1921).—Tabular presentation is given of the vol., total N, total S, total  $SO_2$ , sulfate  $SO_4$ , ethereal  $SO_3$ , neutral S as  $SO_4$ , and NaCl of the urine of 3 patients before and after the administration by intramuscular injection of 10 cc. of a 1% soln. of S in olive oil. The results indicate that there occurs under these conditions an increased destruction of body protein which is shown by the increased N and S excretion. The % of sulfate  $SO_4$  in the form of neutral  $SO_3$  is markedly lowered. The NaCl excretion is greatly increased immediately following the injection. After the second day it decreases as does the vol. of urine, and at this time glucuronuria and urobilinuria appear. The increased S excretion is much greater than the amt. of S injected. The study shows that marked differences exist between the effects of the oral and parenteral administration of S as detd. by the compn. of the urine. F. S. HAMMETT

Blood changes following oral sodium chloride administration. G. SAMSON. *Biochem. Z.* 118, 55-60(1921).—The administration of massive amts. of NaCl by mouth to normal men causes an absolute, as well as a percentage, increase in the serum Cl. However, the greater part of the NaCl is taken up by the tissues. The blood vol. increased regularly through the passage of  $H_2O$  from the tissues into the blood stream. This occurs even when no  $H_2O$  is ingested. There also takes place a simultaneous passage of protein from tissues to the blood. F. S. HAMMETT

Studies on the actions of poisons. The action of quinine on invertase. PETER RONA AND ERNST BLOCH. *Biochem. Z.* 118, 185-212(1921).—These studies show that quinine acts as a poison to invertase and to paramacia. This toxic action is exerted by the free alkaloid base. The degree of the retardation by quinine-HCl is dependent on the H-ion concn.; if this is increased the toxic action is increased. The dependence of the toxic action on the quinine concn. tends to follow the law of mass action, as is shown by the curve of the log of the concn. against the log of the retardation effect. This is a straight line. The toxicity is completely reversible and is independent of the temp., enzyme and sugar concn. The quinine derivs., optoquinine, eucupine and vuzin act similarly to quinine, and are similarly affected by the H-ion concn. The retardation effect of optoquinine and eucupine is like that of quinine, that of vuzin and quinidines is markedly greater. F. S. HAMMETT

Observations on the action of calcium deficiency on the surviving frog heart. KARL HANSEN. *Z. Biol.* 73, 191-200(1921).—An intensive physiological analysis of the response of the isolated frog heart to Ca deficiency. F. S. HAMMETT

The dependency of the photoelectric reaction of the frog eye on the surrounding medium. H. BRUCHELT. *Z. Biol.* 73, 205-10(1921).—Perfusion and diffusion expts. with the frog eye showed that the pupillary contraction following illumination does not occur in KCl, BaCl<sub>2</sub>, and MgCl<sub>2</sub>, while in LiCl and NaCl it takes place as with the normal eye in Ringer soln. Sometimes a paradoxical reaction occurred in MgCl<sub>2</sub> soln. Such double reactions occurred regularly in CaCl<sub>2</sub>-treated eyes. F. S. HAMMETT

The action of deacetylated hellebore on the frog heart. ERNST FREY. *Z. exper. Path. Therap.* 22, 54-64(1921).—Deacetylated hellebore produces an acceleration



of the formation of potential cardiac energy so that the extra-systole reaches a higher level than normal, and the heart may go into tetany. F. S. HAMMETT

The fate of quinine in the human organism. KARL RETZLAFF. *Z. exper. Path. Therap.* 22, 65-91(1921).—The results of personal expts. and correlated data from the literature do not justify the idea that the non-effectiveness of quinine in some cases of malaria is due to the habituation of the organism to the drug; rather it can be attributed to an increased destruction by or an altered reaction of the organism to the compd. F. S. HAMMETT

Influence of alcohol on the excretion of "creatinine bodies". A. AMATO. *Ann. clin. med.* 10, 43-59(1920); *Physiol. Abstracts* 5, 568(1921).—Dogs were used as exptl. animals. Administration of 2 g. of alc. per kg. of body wt. caused a decreased excretion of both creatinine and total N, soon followed by a return to normal values. Larger doses of alc. (up to 5 g. per kg. of body wt.) increased the amt. of total N and decreased the amt. of creatinine excreted. JOSEPH S. HEPBURN

Action of the extract of *Bryonia alba* upon the heart and the circulation of the blood. AR. GRADINESCU. Faculté Med., Bucarest. *Bull. sec. sci. acad. Roumaine* 6, 167-70(1920).—Study was made of the roots of *Bryonia alba*, which are used commonly as a hemostatic. One part of the pulverized dried roots was extd. with 2 parts of alc.; and the ext. was evapd. under reduced pressure at a temp. of 45° to 50°. Several exts. were prepd., alc. of 85%, 80%, 70%, and 60% being used; the more dil. the alc., the greater was the content of active principles in the ext. Injection of a large dose of the ext. into the dorsal sac of the frog produced death. If the contractions of the heart were observed for some time after injection of the ext. into the dorsal sac, the beginning of fibrillation occurred as an extra systole visible to the naked eye; before the ventricular systole, deep red and pale pink points appeared, scattered over the walls of the ventricle. These fibrillary contractions were accompanied by a sudden impairment of the heart which denoted the relaxation of the muscular tonus. The vaso-constrictive action of the ext. was found to occur at a concn. of 1:100,000. Perfusion of the ext. through the isolated frog heart first produced a decrease in the amplitude of the cardiac contractions probably due to action on the cardiac muscle; then the cardiac contractions became of full amplitude. With respect to its action on the blood pressure, the ext. produced hypotension in mammals (the cat and the dog). JOSEPH S. HEPBURN

Poison of imori or boje-Triton pyrrogaster. S. MATEUSAKI AND I. KABEDA. *Tokyo Iji Shinji* No. 2064, 455-60; No. 2071, 815-21(1918); *Jap. Med. Literature* 6, 4-5, 10-11(1921).—The poison is present in the skin, muscles, and internal organs, and is obtained most effectively by trituration of the skin with sand and extn. with 10 vols. of glycerol. The resulting ext. is yellowish brown, has a strong odor, an irritating bitter taste, and a faintly alk. reaction, and contains protein. Two distinct toxins are present, a relatively unstable hemolysin, and a more stable neurotoxin which produces death in exptl. animals by paralysis of the respiratory center, directly injures the myocardium, and has a direct anticomplementary action exerted against the thermolabile ingredient of the complement. The poison was found to be far more toxic for warm-blooded animals than for cold-blooded animals. The minimum lethal dose of a 30% diln. of the ext. on intravenous or intraperitoneal injection was: 0.5 to 0.7 cc. per kg. of body wt. for warm-blooded animals, 5 to 8 cc. for frogs, 35 cc. for snakes, and 100 cc. for Triton. The fatal dose by mouth was 100 times that by intravenous injection. The poison produced a local swelling on subcutaneous injection into rabbits; this swelling became indurated, then gangrenous. On intravenous injection into rabbits, it caused accelerated respiration within 3 min.; the respiratory movements became violent, the skeletal muscles weak; the animal fell over after 15 min.; respiration changed to slow and feeble, and ceased after 4 hrs.; hemorrhages occurred in the lungs, liver, stomach, in-



testes, spleen, kidneys, and adrenals. Introduction of the poison into the eye gave rise to a severe conjunctivitis and a slight myosis. The poison was reduced to  $1/4$ ,  $1/10$ , and  $1/100$  of its original toxicity by heating for 30 min. at temps. of  $46^\circ$ ,  $70^\circ$ , and  $106^\circ$ , resp. It was markedly reduced in toxicity by exposure to direct sunlight for 2 hrs. or by evapn. to dryness *in vacuo*, was not influenced by freezing, passed very slowly through an animal membrane, and was destroyed by ultra-violet light, acids, alkalis, 0.5%  $\text{KMnO}_4$  soln., and gastric juice. Filtration through blood charcoal removed the hemolysin but did not affect the neurotoxin. The toxicity of the neurotoxin was lessened by passage of  $\text{CO}_2$  or  $\text{H}_2\text{S}$  into its soln., and was neutralized by suspensions of tissues; suspensions of the organs of the central nervous system were most active, followed by those of glandular organs, while those of muscle and connective tissue were least active. It was not affected by shaking. The hemolysin was destroyed by heating at a temp. of  $56^\circ$  and could not be reactivated. Shaking had no action at the end of 2 hrs., but produced a marked decrease in activity at the end of 24 hrs. The hemolysin was destroyed by  $\text{H}_2\text{S}$ ,  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ , alc., evapn. to dryness *in vacuo*, or exposure to direct sunlight for 2 hrs. The activity was reduced to 25% of its original value by addition of large amts. of  $\text{NaCl}$  to its soln., to 20% of its original value by passage of  $\text{H}_2$  through its soln. for 1 hr., was reduced slightly by 0.5%  $\text{PhOH}$ , was destroyed by that compd. if present in sufficient concn., was reduced to 12.5% of its original value by the action of filtered saliva for 1 hr., and was almost completely destroyed by pancreatin. When  $\bullet$  was passed into a soln. of the hemolysin, the pptd. globulin contained approx. 40% of the lysin, while 60% remained in soln. with the albumin.

JOSEPH S. HEPBURN

Comparative action of histamine and of the extract of hypophysis on the vascular system in conjunction with adrenaline. J. B. LOSA. *Rev. Assoc. Med. Argentina* 1920, Nos. 186-8; *Physiol. Abstracts* 5, 564(1921).—Ext. of hypophysis increased and prolonged the action of adrenaline on the blood pressure; histamine in all doses had an action antagonistic to that of adrenaline.

JOSEPH S. HEPBURN

Action of snake venom on the isolated uterus and intestine of the guinea pig. C. F. VELARDE AND J. MIRAVENT. *Rev. Assoc. Med. Argentina* 1920, Nos. 186-8; *Physiol. Abstracts* 5, 576(1921).—The venom of serpents produces contraction of the isolated uterus and intestine of the guinea pig. The power to produce contraction of these organs is not connected with the hemolytic action or coagulating action, and does not always run parallel to the toxicity.

JOSEPH S. HEPBURN

Emetine kerato-conjunctivitis. C. OGUCHI. *Tokyo Iji Shinji* No. 2056, 17-8 (1918); *Jap. Med. Literature* 5, 26(1920).—Instillation of an aq. soln. of emetine of a concn. exceeding 1% produced keratitis and conjunctivitis, but only after the lapse of approx. 24 hrs. The emetine possibly acted by producing congestion and transudation from the pericorneal vessels, thereby giving rise to edema of the cornea and finally to ulceration.

JOSEPH S. HEPBURN

Capillary poisons and shock. H. H. DALE. *Lister Inst. Bull. Johns Hopkins Hosp.* 31, 257-66(1920). Anaphylaxis. *Ibid* 310-19. Chemical structure and physiological action. *Ibid* 373-80.—Herter lectures, Johns Hopkins Univ. A review. A. P. LOTHROP

Chemical stimulation and chemical contraction in striated muscle. JOSEF WILMERS. *Arch. ges. Physiol.* 178, 193-213(1920).—The mode of action of various chem. substances upon non-curarized sartorius muscle (frog) was detd. The muscle was fixed in the middle, each end being attached to a recording lever. But one end of the muscle was subjected to the direct action of the chemical. If only this portion of the muscle contracted it was assumed that the action of the chemical was direct and localized. If the entire muscle contracted it was assumed to be the result of a true stimulation. Solns. such as isotonic  $\text{Na}$  oxalate, and  $\text{Na}$  phosphate mixtures, which induce a fibrillar twitching, caused both segments to contract, thus indicating a true stimulation.



HCl in various concns., NaOH, ammonia, alanine, MeOH, EtOH, PrOH,  $\text{CHCl}_3$ , bile, and the cutaneous secretion of the frog, all substances which cause a smooth contracture, exerted an effect upon the immersed portion only. Other substances, as hypertonic Ringer soln., isotonic Na citrate, and  $\text{Na}_2\text{SO}_4$  solns. caused a reaction-complex exhibiting characteristics of both types of reaction.

G. H. S.

The contracting surviving heart-strip preparation. III. Proprioceptive tonus reflex of the frog heart and its sensitization by heart glucosides. PAUL, WICHELIS. *Arch. ges. Physiol.* 179, 219-32(1920).—Digitoxin in concns. of  $0.7-3 \times 10^{-4}$  caused a slight increase in the amplitude of contraction and an insignificant retardation in frequency of contraction of strips of heart muscle. After an interval of 15-17 min. diastolic arrest occurred. This relative lack of specific activity is manifested with either auricular or ventricular muscle. When a strip of auricle is treated with digitoxin in concn. of  $1.5 \times 10^{-3}$  for 30 min. and then subjected to sudden tension, an instantaneous change from diastole to max. systole occurs. The ventricular muscle fails to react in this manner unless it is joined to a strip of muscle containing ganglia. Narcotics—chloral hydrate, cocaine—inhibit this reaction. Chloral hydrate ( $2-4 \times 10^{-4}$ ) not only prevents the systolic contraction but destroys the excitability of the muscle. Treatment with cocaine also prevents the systolic contraction. When the strip, subjected to the action of digitalis, is treated with cocaine ( $2-6 \times 10^{-4}$ ) and then stimulated mechanically the systolic contraction suddenly, or gradually, undergoes a transition to diastolic arrest. Certain of the expts. indicate that digitalis acts upon the ganglionic elements of the heart and that it also sensitizes the reflex app. The antagonism between digitalis and cocaine is likened to the antagonism between tetanus toxin and cocaine.

G. H. S.

Actions of various substances in partial heart block, with experiments on the origin of heart block through the action of oligodynamic metals. A. A. J. VAN EGMOND. *Arch. ges. Physiol.* 180, 149-208(1920).—Partial heart block was produced in the isolated rabbit heart, perfused with Locke-Ringer soln., by mechanical pressure on the bundle of His, by the application of formalin or  $\text{AgNO}_3$ , or more simply, by merely touching the bundle with a piece of Cu. Apparently contact with the metal is effective through the small amt. which goes into soln. Cd and Zn were also active, while Pb, Al, Bi, and Ag showed a much weaker action. A heart subjected to such a block later returns to its normal rhythm. Spontaneously induced heart block, by the use of impure Ringer soln., does not again regain normal rhythm. Various therapeutic agents were applied to the partially blocked heart. Strophanthin hastened the therapeutic stage of conduction between auricle and ventricle. Conduction is increased by strychnine, even in amts. which have no effect upon the frequency or size of the contractions. In larger amts. other effects were observed.  $\text{CaCl}_2$  in small amts., exerts a favorable influence upon conductance with a simultaneous improvement in contractility. With larger amts. conduction was diminished in the blocked, as in the normal heart.  $\text{BaCl}_2$  always impaired conductance between auricle and ventricle and intensified the block. Adrenaline was practically without effect. Caffeine disturbed conductance. Camphor in large amts. and physostigmine in small amts. impaired conductance. Very small amts. of camphor showed an irregular reaction, but physostigmine in high dilution markedly lengthened the block, or absolutely destroyed conductivity.

G. H. S.

The chemistry of neosarsphenamine and its relation to toxicity (RAIZISS, FALKOV-17.

## I-ZOOLOGY

R. A. GORTNER

Notes on chemotropism in the house fly. I. R. SPERRY. *Ann. Appl. Biol.* 7, No. 1, 124-40(1920); *Expt. Sta. Record* 44, 454-9.—S. concludes that "essential



oils are unattractive to the house fly in general. Certain essential oils evoke negatively chemotropic stimuli, these being oil of *Pinus sylvestris*, orange oil, lemon oil, citronella oil, oil of juniper berries, and possibly camphor oil. Certain essential oils are inactive in raising stimuli, these being cedar oil, eucalyptus oil, and oil of bitter almonds. They may themselves be neither positively nor negatively chemotropic in action but probably have slight negative features. During evapn. the repellent actions pass off, soonest in orange oil and later in lemon oil, citronella oil, and oil of *P. sylvestris*, and some co-ordination may occur in relation to the rate of evapn. and the retention of repellent qualities."

H. G.

Variations in the total, amino, and ammoniacal nitrogen and water content of the hen egg during incubation. A. AGGAZZOTTI. *Arch. Sci. Biol.* 1, 120-47(1919); *Physiol. Abstracts* 5, 139-40(1920).—The concn. of both the total and the amino N increases during incubation of fertile eggs as a result of the desiccation of the white. A similar, though smaller, increase in both forms of N occurs during incubation of infertile eggs. The concn. of  $\text{NH}_3$  in the white increases during the first half of incubation and decreases during the second half of incubation of fertile eggs, and increases slightly during incubation of infertile eggs; the increase may be due to desiccation, the cause of the decrease is unknown. The concn. of free amino N increases during incubation with respect to both the original and the dry substance, i. e., undergoes an actual increase independent of desiccation of the white. The concn. of the water decreases in the white of fertile eggs as incubation progresses, but remains unchanged during the last days of development; a similar, but less marked, decrease in the moisture content of the white occurs in the infertile eggs. Both the total N and the amino N of the yolk decrease slightly in concn. but remain unchanged in amt. during incubation of fertile eggs until the last few days; then they increase; the decrease in concn. is due to diln. of the yolk; the final increase is attributed to the passage of fetal nitrogenous products into the yolk. During incubation of infertile eggs, both the total N and the amino N of the yolk show a slight decrease when calcd. on the original basis, but not when calcd. on the dry basis. The concn. of the  $\text{NH}_3$  in the yolk of fertile eggs increases during incubation when calcd. on the dry basis, but decreases toward the end of incubation independent of the diln. of the yolk. The free amino N of the yolk decreases in concn. during incubation. The water content of the yolk increases during incubation especially during its middle period; this is true of both fertile and infertile eggs. Changes in the reaction of both the white and yolk during incubation are probably due to changes in the concn. of the amino acids. The embryo probably can utilize the products formed in the hydrolysis of the egg proteins.

JOSEPH S. HEPBURN

Coloration of Haematozoarius by methylene blue. F. VERGARA. *Mem. rev. soc. cient. Antonio Alzate* 37, 397-9(1921).—The addition of a 20% soln. of  $\text{K}_2\text{Cr}_2\text{O}_7$  drop by drop to a satd. soln. of methylene blue in  $\text{H}_2\text{O}$  is continued until pptn. is complete, after which the ppt. is filtered off, washed with  $\text{H}_2\text{O}$ , dried and powdered. A soln. of 0.02 g. of the powder in 10 cc. of  $\text{MeOH}$ , with a few mg. of eosin, gives a coloration much resembling the Leishmann stain, the technic being the same. M. R. SCHMIDT

The pigment of the hepato-pancreas of the crayfish. I. LEWIN AND E. STENGER. *Arch. ges. Physiol.* 178, 80-90(1920).—The hepato-pancreatic glands of the crayfish secrete enzymes which are active upon proteins, carbohydrates, and fats. Within the glandular tissue a granular pigmented substance is found. The yellowish brown secretion obtained from the organ shows, when perfectly fresh, a continuous spectrum but upon standing for a short time the material assumes a darker and reddish brown color. When in this state it shows a distinct absorption band in the green. Av. detns. show  $\lambda = 560\mu$ . Shaking with air or contact with  $\text{H}_2\text{O}_2$  results in a disappearance of the absorption band, which, however, can be restored by reduction with ammonium sulfide.



Apparently the pigment is unrelated to the blood pigments, to their derivs. or to chlorophyll. The secretion gives protein reactions and contains Fe. When removed from the glands various chem. and physical changes take place. Some of the chem. characteristics of the secretion, together with the reactions of the material when exposed to air, suggest that it may play some part in gaseous interchange within the body. In the blood of the crayfish there is apparently no hemocyanin, and but a small amt. of Cu; 0.01 mg. in the total blood vol. of an animal. G. H. S.

**The occurrence of manganese in land and fresh-water Mollusca.** A. E. BOYCOTT. *Naturalist* 1917, 11-8, 69-73.—The soft parts of 56 species of British land and fresh-water Mollusca were analyzed for Mn colorimetrically. Results are expressed in pts. per 10,000 of dry material. The amts. found range from less than 0.5 pt. up to 270 pts. in a land snail (*Limax arborum*). Most of the Mn seems to be localized in the liver and skin. Some species tend to accumulate Mn from their food and surroundings, but local conditions are able to cause considerable variations in different individuals of the same species. Analyses were made for Mn in a number of plants which snails might or do eat, yielding a range from none in the potato and less than 0.2 pts. in ash leaves up to several hundred pts. in green slime from streams and 690 pts. in a moss from the floor of a culvert. Water plants in general contain more than land plants, and lower plants, except fungi, more than higher ones. E. T. WHERRY

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

**The chemistry of foodstuffs in 1917 and 1918.** H. KUTTENHEULER. *Chem. Ztg.* 43, 841-3, 853-6, 869-70, 889-90 (1919); *Expt. Sta. Record* 43, 563.—This is an extensive review of the literature on food chemistry published in 1917 and 1918.

H. G.

**Report on the work of inspectors of foods for the year 1918-19.** A. W. J. MACFADDEN. H. M. Stationery Office. *Analyst* 45, 243-4 (1920).—"Extract from the annual report of the Medical Department of the local government board for 1918-19." Inspection of imported meat is discussed. Mfrs. of baking powder have successfully safeguarded their products with respect to As. Reform is necessary in the inspection of home-killed meat and in supervision of places where food is prepd. or kept for sale for human consumption. (Cf. *C. A.* 14, 2034.) H. A. LEPPER

**Report of the chemical division.** M. O. JOHNSON AND K. A. CHING. *Hawaii Sta. Rept.* 1919, pp. 40-42; *Expt. Sta. Record* 44, 15-6.—Satisfactory results on a semi-commercial scale have been obtained in the drying of Hawaiian food products by the use of a large tower drier holding trays 3 ft. wide by 4 ft. long. A blower driven by a small gasoline engine forces air around steam coils and up through the trays in the tower. Data are given on the extent of removal of moisture from various vegetables and fruits by this method. Avocado and papaya fruit have been preserved by placing the peeled fruit cut in small cubes in sterilized jars and filling the jars with an ordinary com. tomato cocktail sauce heated to boiling. It has been found possible to utilize pineapple juice in the prepn. of jelly and of vinegar. For the former, equal parts of clarified pineapple juice and guava ext. are used, or pectin pptd. from guava ext. by alc. is added to the pineapple juice before boiling down. The juice can be concd. by freezing and sepg. by centrifugal action. In prepg. vinegar from pineapple juice, the juice testing 11° Brix was sterilized, cooled, and inoculated with ordinary yeast. After standing 5 days the sample showed an alc. content of 5%. The clear juice was then decanted and mixed with a fairly active cider vinegar in the proportions of 1 part of vinegar to 4 or 5



parts of the juice. When tested 2½ months later the 1:4 mixt. contained 4.2% of AcOH and proved to be a vinegar of fine quality. H. G.

**Work of the chemist in the food industries.** L. M. TOLMAN. *Chem. Age* (N. Y.) 27, 241-5(1919).—A brief summary of the development of chem. control in the manuf. of food. H. G.

**The chemist in the packing and allied industries.** CHARLES H. MACDOWELL. *Chem. Age* (N. Y.) 29, 217-23(1921). E. H.

**Colloidal chemistry and food chemistry.** W. OSTWALD. *Chem. Ztg.* 43, 829-31, 849-50(1919); *Expt. Sta. Record* 43, 609; cf. *C. A.* 14, 1166.—This is a discussion of the application of colloidal chemistry to various problems of food chemistry, with particular reference to the chemistry of milk, meat, and bread. H. G.

**Miscellaneous food analyses.** A. E. VINSON AND C. N. CATLIN. *Arizona Sta. Rept.* 1918, 345, 346; *Expt. Sta. Record* 43, 764.—Analyses of barley flour are reported, as well as findings with samples of corn meal and cocoa suspected of contg. ground glass. H. G.

**Food poisoning.** W. L. DODD. *Am. Food J.* 15, No. 5, 20-2, 32(1920); *Expt. Sta. Record* 43, 458.—A general discussion. H. G.

**The theory and practice of cold storage.** M. GREMPE. *Wärme u. Kälte-Techn.* 22, 52-4(1920); *Chimie et industrie* 5, 707(1921).—A discussion of the effects of refrigeration on foodstuffs and of the best methods of application. A. P.-C.

**Antiseptic action of spices in preserved foods.** JEAN LAHACHE. *L'industrie française conserve* 5, 211-14(1919); *Bull. Agr. Intelligence* 11, 126.—Black pepper, cayenne, and ginger prevented fermentation and putrefaction for only a very short time. Mustard, cinnamon, and cloves (whose antiseptic principles are their essential oils) are much more effective, being powerful even in the small quantities used in food and decidedly stronger than chem. antiseptics. This work is in its infancy and will be continued. H. A. LEPPER

**Bacteriological examination of tomato products.** E. BERTARELLI AND M. MARCHELLI. *Ann. igiene* 30, No. 6, 303-22(1920); *Expt. Sta. Record* 44, 11-12.—The authors discuss the relative merits of the Howard method (U. S. Dept. Agr., *Burr. Chem. Circ.* 68, 14) and the direct-count method as described by Vincent (*J. Bact.* 3, 183-5 (1918)) for the examn. of tomato products for content of bacteria, molds, etc. While the Vincent method is considered superior to the Howard, the possibility of errors in both are thought to be considerable. As a substitute method a procedure is recommended which is essentially as follows: Two cc. of the tomato product is made up to 50 cc. with distd. water, shaken thoroughly, and filtered through four thicknesses of muslin. The residue is carefully washed with another 50-cc. portion of distd. water and the filtrate collected in the beaker contg. the original filtrate. The combined filtrate is estd. to contain all but about 20% of the bacteria originally present, and in estg. the bacterial count a correction is made for this. By careful manipulation 1 cc. portions are dropped from a pipet on glass slides, spread over the surface with a Pt wire, fixed with alc.-ether, stained with Loeffler's blue, and subjected to microscopic count in the usual way. With the use of this method a number of samples of Italian tomato products were examd. and compared with the United States standards for bacterial count. A study was also made of the effect on the content of bacteria and molds of different temps. during the prepn. of the product and of length of storage. The data obtained in this study indicate that, as far as bacteria are concerned, it is not necessary to sterilize the product completely. Mold growth, however, was quite extensive in the products which had not been completely sterilized. For this reason the use of sound, thoroughly washed tomatoes is urged. H. G.

**Commercial possibilities of dehydration.** HENRY W. BANKS, 3RD. *Am. Food*



J. 16, No. 4, 7-9; No. 5, 10-11(1921).—The com. possibilities of dehydration are discussed with the important influencing factors. Various methods of drying foods, including the mechanical app., are described.

H. A. LEPPER

**Methods of preparing vegetables for dehydration.** P. F. NICHOLS AND C. R. GROSS. *Chem. Age* (N. Y.) 29, 139-41(1921).—Different procedures of blanching by immersion were compared with steam blanching of carrots, cabbage, and potatoes prior to dehydration. Products equally attractive can be prepd. by the former procedure, which is the more easily controlled.

H. A. LEPPER

**Effect of heat on different dehydrated vegetables.** C. E. MANGELS AND H. C. GORE. U. S. Bur. Chem. *J. Ind. Eng. Chem.* 13, 525-6(1921).—The effects of the degree of temp., time of exposure to the temp. and of the relative humidity of the surrounding air on the quality of the dehydrated onions, turnips, celery, tomatoes, cabbage, white potatoes, carrots, string beans, sweet corn, and sweet potatoes, were studied. The first 5 are easily injured, the next 4 fairly resistant and last one is very resistant. As temp. increases, the exposure necessary to cause injury decreases. Exposure in an atmosphere of comparatively high relative humidity at a lower temp. appears more injurious than the same exposure in a dry atmosphere.

H. A. LEPPER

**The relation of moisture content to the deterioration of raw-dried vegetables upon common storage.** H. C. GORE AND C. E. MANGELS. U. S. Bur. of Chem. *J. Ind. Eng. Chem.* 13, 523-4(1921).—Raw-dried vegetables deteriorate on storage in air-tight containers at ordinary temp. unless the H<sub>2</sub>O content is below a certain point. The critical H<sub>2</sub>O content, below which changes in color and flavor are well retained for 6 mo., are carrots 4.90-7.39, turnips 5.00, onions 5.74-6.64, spinach 3.81-5.38, cabbage 3.00-3.34%.

H. A. LEPPER

**The composition of vegetables and their waste products.** M. F. VON SCHLESNITZ. *Landw. Jahrb.* 52, No. 2, 131-278(1918); *Expt. Sta. Record* 43, 63.—For the purpose of detg. which vegetables should be considered as foods and which as luxuries, extensive analyses have been made of the edible portion, of the kitchen waste, and of the garden waste of the common vegetables. These analyses are assembled in the following tables: Proximate analyses of the vegetables in terms of the dry and the fresh material, proximate analyses of the garden waste in percentage of the dry and of the fresh material, proximate analyses of the kitchen waste calcd. to the same basis, and the wt. in g. of the edible portion, and of the kitchen waste in 1 kg. of the vegetables as marketed.

H. G.

**Food value of asparagus.** P. JUQUELIER. *Industrie française conserve* 5, 137-40 (1919); *Bull. Agr. Intelligence* 10, 810.—The analysis of asparagus gave H<sub>2</sub>O 93.32, nitrogenous matter 1.98, fat 0.28, carbohydrates 2.74, mineral 0.54 and cellulose 1.14%. Compared quant. 100 g. of asparagus are equivalent to potatoes 16.46, peas 35.95, artichoke 74.27, and lettuce 85.46 g. while 100 g. of asparagus yield 13.51 calories compared with 69.35, 37.66, 18.16, 15.80 for the above vegetables in the order named. These figures show that asparagus cannot be considered a really nourishing dish. No substance is found in sufficient proportion to warrant its being regarded as of special value. It is not a plastic food since its total of the ternary constituents is less than 3%. Ash is largely acetate and phosphates of K but their quantity and assimilability do not make them worthy of note. Use of sauce makes the dish of asparagus of more value to the diet.

H. A. LEPPER

**Contribution to the study of the composition of maize.** N. PASSERINI. *Bol. soc. ital. studio aliment.* 1, No. 1-3, 17-22(1919); *Expt. Sta. Record* 44, 359.—Proximate analyses and N detns. of 8 varieties of Indian corn from different sources are reported.

H. G.

**Some vanillin oxidation products: Methods of analysis which exclude them.** W. G. BOWERS AND J. MOYER. *N. Dakota Sta. Spec. Bul.* 5, No. 16, 518-20(1920);



*Expt. Sta. Record* 43, 314-5.—The authors discuss the behavior of vanillin with some of the common oxidizing agents, and suggest a method of detg. the true value of vanillin which is thought to be more accurate than the official method. The method proposed involves the use of the clarifying agent of Folin and Denis (*C. A.* 7, 1769) and the coloring agent of Estes (*C. A.* 11, 675). The technic is as follows: Add 75 cc. of water and 4 cc. of Pb acetate soln. (contg. 5% basic and 5% neutral Pb acetate) to 5 cc. of the vanilla ext. in a 100-cc. flask. Make up the soln. to 100 cc., filter, and place 10 cc. of the filtrate in a 50-cc. flask. To this add 15 or 20 cc. of water and 0.3 cc. of the Estes reagent (Hg dissolved in twice its wt. of concd.  $\text{HNO}_3$  and diluted with 25 times its wt. of water). Treat a 1-cc. portion of the 1% standard vanillin in the same manner and then place both flasks in boiling water for 20 minutes, make up to vol., filter if necessary, and compare in a colorimeter.

H. G.

**Detecting artificial color in jams and jellies.** C. H. CAMPBELL. *Canner* 51, No. 15, 37(1920); *Expt. Sta. Record* 44, 115.—As a method for detecting the addition of more highly colored juices of other fruits to produce a more satisfactory color in jams and jellies made from inferior materials, C. suggests testing a strong soln. of the product with Pb acetate soln. The color of both the ppt. and filtrate is thought to be an indication of the purity of the product. A table is given of the colors produced with Pb acetate and jellies of known compn.

H. G.

**Preparation of sweet potato sirup.** H. C. GORE. *Chem. Age* (N. Y.) 29, 151-3 (1921).—The procedure for the prepn. of sweet-potato sirup is described, including the selection of potatoes and malt, blanching, cooking, reducing to a pulp, mashing with malt, pressing and refining. The yield is about  $\frac{1}{3}$  the wt. of the potatoes used. The process appears to be economically practicable.

H. A. LEPPER

**Manufacture of sweet-potato flour by the "flake" process.** C. E. MANGELS AND S. C. PRESCOTT. *Chem. Age* (N. Y.) 29, 132-5(1921).—The "flake" process, successfully used for making flour from white potatoes, is not applicable to the sweet potato. The slightest trace of injury of the potato produced a green color in the flour. The use of  $\text{NaHCO}_3$  did not prevent its formation. The presence of potatoes infected with black rot imparted a bitter flavor to the finished product. The flour even when of desirable color and flavor is very hygroscopic and hardens to a gummy cake on storage. Losses during cooking make the yield much less than theoretical. Extensive modifications in the process are necessary before it can be used to manuf. sweet-potato flour.

H. A. LEPPER

**Potato flour, a new American industry.** OSCAR JAMES VOGL. *Am. Food J.* 16, No. 5, 12-13, 30(1921).—The process of manuf. of potato flour is described and its economic aspects are discussed.

H. A. LEPPER

**Lupines in human nutrition.** A. FUNARO AND L. MUSANTE. *Atti r. accad. econ. agr. Georg. Firenze* (5) 15, No. 1-4, 68-78(1918); *Expt. Sta. Record* 43, 458.—Analyses of flour prepd. from the common lupine before and after the extn. of the alkaloidal principles by alc. acidified with HCl are reported. These indicate a slight increase in fat, protein, cellulose, and pentosans and a decrease in other carbohydrates and in mineral matter. The high percentage of sol. proteins in lupine flour is thought to make it a valuable part-substitute for wheat flour, 15 parts of the lupine flour to 85 of the wheat flour being suggested as satisfactory proportions.

H. G.

**The chemical engineer in biscuit manufacture.** JULIUS ROHN. *Chem. Age* (N. Y.) 29, 129-31(1921).—"A survey of the requirements, responsibilities and opportunities of the chemically trained man in the baking industry."

H. A. LEPPER

**Bread making with lime water; its interest from the point of view of colonial hygiene.** A. LAHILLE. *Bull. inst. sci. Saigon* 1, 136-41(1919); *Bull. Agr. Intelligence* 10, 811-12.—Expts. in bread making with lime water carried out at Saigon are given



in detail. Physical and organoleptic characters of bread are improved. In greater part, the colonies only traces of CaO are found and vegetation and drinking H<sub>2</sub>O are only slightly calcareous. Deficiency for adults is 0.35-0.40 g. CaCO<sub>3</sub> per day. L. recommends adding CaO to bread to make up this deficiency. H. A. LEPPER

Fat determination in dehydrated potatoes. O. MATZDORFF AND W. KÖHNE. *Chem. Ztg.* 44, 103(1920); *Expt. Sta. Record* 43, 414; cf. C. A. 15, 560.—Detns. of the fat content of various com. products of dehydrated potatoes before and after hydrolysis of the starch are reported. While the results in general were higher after hydrolysis of the starch, one or two were lower. The authors conclude that the fat content is so low in dried potato preps. that accurate results can not be expected in this detn. H. G.

Whale meat. H. A. MATTILL. *California Sta. Rept.* 1919, p. 58; *Expt. Sta. Record* 42, 861.—As the result of artificial digestion expts., it is reported that whale meat is as easily digested as any other meat. Raw whale meat was not so completely digested at the end of 2.5 hrs. as raw beef, but more completely digested than the beef in 4 hrs. In the cooked condition it was rather more quickly and completely digested than beef. The compn. of whale meat is reported as follows: Water 71.22%, ash 1.2, protein 23.13, fat 4.24, and undetd. 0.21%. H. G.

Frozen meat. MARTEL. *Bull. acad. med.* 81, 585(1919); *J. pharm. chim.* 20, 62-8; *Bull. Agr. Intelligence* 10, 1016-9.—Frozen meat submitted to -10 to -15° is to be distinguished from refrigerated meats, cooled down to +4 to -1°. Changes in both kinds of meat are discussed from literature and previous work. H. A. LEPPER

The protection of meat commodities against blowflies. R. A. WARDLE. Univ. Manchester, England. *Ann. Applied Biol.* 8, 1-9(1921).—This investigation was undertaken to find some method of preventing oviposition by blowflies on foodstuffs. Two factors are concerned in oviposition; the nature of the foodstuffs attacked and meteorological conditions. Blowflies are attracted to a wide range of substances, but oviposit, by preference, on substances containing animal proteins, particularly albumins and globulins. Albumoid substances such as gelatin and skin are not attractive. Protein which has been coagulated by heat or washed with water or salt soln. does not appear to be attractive. Attempts to induce *Calliphora* to oviposit on tripe were unsuccessful. The stimulus for oviposition, whether olfactory or gustatory, probably resides in the exuding juices, blood and muscle plasma, of the food substance. The blood, however, is less attractive than the muscle plasma. Putrifying substances are more eagerly sought than fresh; it was not ascertained what the attractive principle was. Foods exposed to the sunshine were seldom oviposited in, while in the shade, they were readily blown. It is pointed out that this behavior will depend on the response of the blowfly to light; some species, like *Lucilia caesar* are more strongly phototropic while others like *Calliphora erythrocephala* are less so. High atm. moisture favors oviposition; wind is antagonistic. A number of repellent substances were applied to slices of raw kidney or liver, but with no marked success. Samples of foodstuffs were then placed in glass cylinders over the openings of which pieces of cotton twine netting with 1/4 inch meshes were fastened. The blowflies could readily pass through this netting. The repellent substances were smeared upon the netting, the following substances being used: Oil of cloves, aniseed, eucalyptus, almonds, citronella, cinnamon, formic acid, borac acid, picric acid and nitrobenzene. Samples protected with eucalyptus oil, formic acid and sometimes clove oil were untouched for 12 hrs., but were attacked later. Aniseed oil, however, prevented oviposition. It was tried out on a larger scale and in every case gave protection for a 24-hr. period. The aniseed oil was not improved for this purpose by diln. with alcohol or emulsifying with soap. CHAS. H. RICHARDSON

Castor bean poisoning. T. MORESCHE. *Clin. vet.* 42, No. 21-22, 621-8(1919);



*Vel. Rev.* 4, No. 1, 62, 63(1920); *Expt. Sta. Record* 43, 78.—M.'s expts. show castor beans to be poisonous for carnivores as well as herbivores. The lesions induced by feeding the seeds are mainly intense hemorrhagic inflammation and local necroses of the mucous membrane of the stomach and intestines, marked renal congestion, and hyperemia of the spinal medulla and brain. Feeding expts. led to the conclusion that the poisonous principle is located in the kernel of the seeds and not in the coverings. Since the toxic principle of the seeds could not be extd. with ether, it is concluded that it cannot be due to the oleoricin contained in the oil.

H. G.

**Olive investigations.** W. V. CRUESS AND J. R. ZION. *California Sta. Rept.* 1919, 41, 42; *Expt. Sta. Record* 42, 805.—A study of the control of color in ripe olives is reported. The darkest and best color was obtained when the lye used did not exceed 3% or fall below 1%, and when the first treatment barely penetrated the skin. Exposure after the second lye treatment did not increase the color. Slight alkalinity of the brine in the cans (not over 0.01%) increased the color, while acidity bleached it. The use of enameled cans was found to be favorable to the stability of the color, while plain tin injured the color and clouded the brine. A study by Cruess of the functions of lye during the various stages of olive processing has been previously noted from another source (*C. A.* 15, 129), as has also the description of a new process of olive pickling by the use of heated, aerated, and circulating liquids (*Calif. Sta. Bull.* 289, 195-200 (1917)). A process by which the disagreeable odors and flavors of inferior olive oil can be removed has been developed by Cruess and C. C. Scallione. The process consists of treating the oil at from 185 to 190° F. with about 0.1% of soda ash, from 2 to 5% of fine bone-black, and a stream of CO<sub>2</sub>, after which the oil is cooled and filtered. In cooperation with A. W. Christie it has been found that olive pomace contains from 6 to 14 % of oil, which may be recovered by means of solvents such as gasoline, and used in soap making.

H. G.

**A bacteriological study of ripe olives.** R. C. ROSENBERGER. *N. Y. Med. J.* 112, 222-5(1920); *Expt. Station Record* 44, 558.—This is the report of a bacteriol. examn. of over 250 samples of ripe olives. The study was made under the auspices of the Dairy and Food Commission of Pennsylvania following outbreaks of botulism. No evidence of *Bacillus botulinus* or its toxin was found in any of the olives examd., although many other organisms were present in all preps. Inoculation of sterile ripe olives with a strain of *B. botulinus* resulted, after anaerobic culture, in the development of a rancid offensive odor.

H. G.

**Darso.** M. A. BRESON AND A. DAANE. *Oklahoma Sta. Bull.* 127, 19(1919); *Expt. Sta. Record* 43, 137.—Darso, a grain sorghum of unknown origin, is regarded as a probable cross between a saccharine and a nonsaccharine sorghum. It is described as a leafy, stocky sorghum, red-seeded, drought-resistant, early maturing, and very uniform in height. Analyses made by the station showed that darso contained a higher percentage of total sugars than was found in kafir or feterita. The chem. compn. of the grain and of the forage proved to be very nearly the same as that of the grain and forage of Blackhull White kafir. The results of a single feeding test with hogs, by C. T. Dowell, seemed to indicate that in feeding value darso is not equal to Blackhull White kafir. A digestion expt. with sheep showed that the nutrients from the two plants were about equally digestible.

H. G.

**The detection of agar-agar.** ALBERT E. PARKES. *Analyst* 46, 239-40(1921).—Stir 50 g. raw fruit pulp and 100 cc. of warm H<sub>2</sub>O or 50 g. of jam and 500 cc. H<sub>2</sub>O at 50° until disintegrated. Allow to settle and filter, using alumina cream if necessary. Wash with warm water. Boil the filter and ppt. with 50 cc. H<sub>2</sub>O, and filter again. If the filtrate does not gel on cooling evap. to small vol. Ignite the residue on the filter and exam. the ash insoluble in HCl for diatoms.

NICHOLAS V. S. MUMFORD



. Historical notes on cotton seed as food. ICIE G. MACY. *J. Dairy Sci.* 4, 250-65 (1921).—A review of the use of cotton seed as food with special attention to the use of press-seed cake as a feeding stuff and the problem of its objectional properties.

H. A. LEPPER

Gossypol in cottonseed meal. W. A. WITHERS. *North Carolina Sta. Rept.* 1919, 40, 41; *Expt. Sta. Record* 43, 411.—In continuation of the study of gossypol, the toxic principle of cotton seed, by Withers and Carruth (*C. A.* 12, 838), and by Carruth (*C. A.* 12, 905), the results of a further investigation of its chem. properties and the possibilities of its removal from cottonseed meal are reported. No evidence was obtained that gossypol or D-gossypol is left in the meal after extrn. with  $\text{Et}_2\text{O}$  and then with aniline. The aniline-gossypol and the aniline-D-gossypol contained, resp., 73.74 and 74.81% of C, 5.76 and 6.12% of H, and 3.85 and 3.89% of N. Aniline-D-gossypol on heating to  $140^\circ$  in the air gained 0.71% in wt., while aniline-gossypol gained 1.96%. These results are considered to furnish a further proof that the two substances are not identical. Cottonseed hulls were found to contain 0.75% and the meats 0.7% of gossypol. Benzidine, aniline, phenylhydrazine, *p*-nitroaniline, *p*-toluidine, and  $\alpha$ -naphthylamine all produced ppts. with the gossypol present in crude cottonseed oil. These reagents and urea in alc. soln. did not, however, form ppts. with pure gossypol or D-gossypol. Free gossypol or D-gossypol in alc. soln. formed ppts. with the alc.-sol. proteins of either wheat flour or cottonseed meal. This is thought to explain partially why heating reduces the toxicity of cottonseed meal, on the assumption that the gossypol or D-gossypol protein compd. is not readily digested by the animal. In general, heating cottonseed meals to various temps. in atm. of different gases and in the presence of various amts. of water decreased the gossypol but increased the D-gossypol content, although the results obtained have not been consistent in all cases.

H. G.

Milk in the tropics. R. J. BLACKHAM. *Lancet* 1920, II, 1130-40.—The most of the milk supply in the tropics comes from the cow and the buffalo. The private milk supply is highly adulterated and largely contaminated. In an analysis of 326 samples of milk in India it was found that cow milk was uniformly up to and buffalo milk uniformly below, the standard laid down for India by various writers. Special attention was paid to the compn. of buffalo milk and the av. result of analyses of 124 samples was as follows: Sp. gr. 1.0304, total solids 15.9, fat 5.9, non-fatty solids 10.0. Buffalo milk contains about twice as much fat as cow milk. Both in England and in India the bacterial content of milk is often greater than that of sewage. The soln. of the milk problem in India is the development of some substitute for fresh milk such as dried milk powder, which can be prepd. under hygienic conditions, contains all the chem. constituents of fresh milk, and can be kept indefinitely in a dried state. Its digestibility is good and it is suitable for infant feeding.

E. B. FISK

Studies in milk secretion. VI. On the variations and correlations of butter fat percentage with age in Jersey cattle. J. W. GOWEN. *Genetics* 5, No. 3, 249-324 (1919); *Maine Sta. Bull.* 284, 291-6; *Expt. Sta. Record* 44, 178; cf. *C. A.* 14, 2508; 15, 128.—This is an elaborate biometrical study of the percentages of fat in the milk produced during the first eight months of 1,713 lactations in a well established Jersey herd. The methods of treatment were the same as those employed in Study V (*Genetics*, 5, 111-88(1923)), which dealt with the milk records of this herd. It was found that the butter fat percentage decreased slightly with age, and on the assumption that the decline is uniform this relationship is expressed by the formula  $f = 5.332 - 0.0191x$ , where  $f$  is butter fat percentage and  $x$  is the age in years at the beginning of lactation. At the greater ages the observed means show considerable dispersion from this line owing, it is thought, to paucity of data. Generalized probability curves were fitted to the frequency distributions of each age, and an extensive series of coeffs. is presented showing



the correlations between the fat percentages of different lactations taken singly or in groups. These coeffs. are deemed useful in estg. the influence of unfavorable environment acting during a particular lactation.

H. G.

**Investigation into milk yield of Ayrshire cows.** J. F. TOCHER. *Trans. Highland Agr. Soc. Scot.* [5] 31, 237-56(1919); *Expt. Sta. Record* 43, 74.—This is a preliminary report of a statistical analysis of the manuscript records of the Scottish Milk Records Assoc. for the years 1911 and 1912. Tables and diagrams are presented to show the relationships of (1) yield of milk and percentage of fat, (2) length of lactation and yield of milk, (3) age of cow and yield of milk, (4) age of cow and percentage of fat, and (5) season of year when parturition took place and yield of milk. The max. amt. of milk per lactation and the minimum percentage of fat occurred at the age of about 10 years. Cows calving from August to November produced more milk per lactation than those calving during other months, but the difference was due entirely to a longer average lactation period. A table showing the frequency distribution of milk yields indicates that half the cows produced more than 6,000 lbs. of milk and 2% more than 10,000 lbs. A frequency table for fat percentages based on this investigation is given in the following abstract.

H. G.

**Variations in the composition of milk.** J. F. TOCHER. *Scot. J. Agr.* 2, No. 3, 343-53(1919); *Expt. Sta. Record* 43, 74.—In 384 mixed-herd samples of milk collected under T.'s supervision the av. fat percentage was 3.495 with a standard deviation of 0.549. The av. percentage of solids-not-fat was 8.85 with a standard deviation of 0.375. In over 11,000 lactation records of Ayrshire cows collected by the Scottish Milk Records Assoc. (see above) the mean percentage of fat was 3.727 and the standard deviation 0.324. "The results of this paper show that the prescribed minima for butter fat (3%) and for solids-not-fat (8.5%) are artificial in character, and are based neither on the real minima found to exist for these constituents nor on an adequate study of the natural variations occurring in genuine milk."

H. G.

**The variability of cow milk.** H. S. H. WARDLAW. *Proc. Linnean Soc. N. S. Wales* 42, IV, 815-65(1917); *Expt. Sta. Record* 42, 875.—The f. p. depression, density, elec. cond., and chem. compn. of samples of afternoon milk from 109 normal cows were studied. Using the ratio of range to mean as the measure of variability, W. finds that depression of the f. p. and density were the least variable quantities measured. Of the chem. constituents, lactose was the least and fat the most variable. The percentages of fat and ash were greater in the milk of older cows, and that of protein less. The other detns. (physical and chem.) were not affected by age. As lactation progressed the percentage of lactose became slightly lower, but the elec. cond. and the percentages of fat and of protein increased.

H. G.

**The influence of calcium and phosphorus in the feed on the milk yield of dairy cows.** ED. B. MINGS AND T. E. WOODWARD. *J. Dairy Sci.* 4, 185-217(1921).—Experimental work on the influence of feed on the milk yield of dairy cows is described and discussed and the results are summed up as follows: Feeding cows for several years according to the commonly accepted standards with little or no additional pasture, may result in reduction of the milk much below the optimum. This condition may be corrected by giving the animal a dry period of 2 mo. with a ration contg. legume hay and grain with a high P content, with 3-4 times the protein required for maintenance and with 2 or 3 times the total nutriment. The subsequent milk yield may sometimes be doubled by this treatment. Yield of cows reduced by several years standard feeding can be increased by feeding "alternated rations with phosphate" during the dry period. This is taken to mean that ordinary rations are more likely to be deficient in one or both of the principal bone-building elements than in any other constituent (cf. C. A. 14, 294). Also in U. S. Dept. Agr., *Bull.* 945, 1-28(1921).

H. A. LEPPER



**The cause of changed milk yields following transfer from pasture to stall feeding.** J. J. O. DE VRIES. *Verslag Ver. Exploit. Proefsuivelboerderij Hoorn 1917*, 22-8; *Expt. Sta. Record* 44, 73.—Eight cows, after being brought into the barn, were fed grass cut from the pasture previously occupied. The av. milk yield in 5 days after the change was 23.3% below the av. daily yield in the 4 days preceding. The amt. of fat was reduced 13.9%, total solids 18.9, protein 26.3, and milk sugar 18.5%. It is concluded that the drop was due to the change in living conditions and not to the character of the feed.

H. G.

**Influence on butter fat of the rice polish in the feed of dairy cows.** A. R. PADMANABHA IYER. *Cent. Provs. and Berar Dept. Agr. (India) Rpt. Agr. Col., Nagpur, Bot. and Chem. Research (etc.)*, 1919, 20; *Expt. Sta. Record* 44, 573.—This is a brief report without exptl. details of a study of the use of rice polish ("rice konda") with a ration of linseed cake and chuni for milch cows. Neither the milk yield nor the fat percentage was changed by the feeding of rice polish, but the sapon., Reichert-Meissl, and Polenske numbers of the butter fat were increased and the I number was decreased. It is concluded that rice polish counteracts the softening effect of linseed cake and thereby permits the production of a good quality of ghee in districts where cottonseed cake is not available.

H. G.

**The relation between the fat-content and the electrical conductivity of milk.** H. S. H. WAROLAW. *Proc. Linnean Soc. N. S. Wales* 43, III, 613-25(1918); *Expt. Sta. Record* 42, 875.—W. reports that the removal of fat from milk increases the elec. cond., the increase being directly proportional to the vol. of fat removed.

H. G.

**Notes on the methylene blue reductase test.** R. B. TENNENT. *Queensland Agr. J.* 13, No. 2, 51-4(1920); *Expt. Sta. Record* 43, 271.—T. reviews some of the work of previous investigators on the methylene blue reduction test, and reports several observations on the rapidity with which the dye was decolorized by milks contg. different numbers of bacteria.

H. G.

**Experiments with the Lobeck biorizator.** W. WBOEMANN. *Arch. Reichsgesundh.* 51, 397-459(1919); *Expt. Sta. Record* 43, 877.—W. reports an extended series of bacteriol. and chem. studies on biorized milk. App. of different models and varied capacities was used. The biorization process had little influence on the chem. characteristics of the milk. There was a slight coagulation of the albumins and globulins, a decrease in the capacity for reducing  $H_2O_2$ , a lowering of the acidity, and a more rapid formation of cream. The taste and odor were improved, and the milk remained sweet twice as long as the raw milk. Milks were inoculated with various organisms including *Bacterium coli communis*, *B. suispestifer*, *B. pyocyaneus*, *B. cyanogenus*, and tubercular organisms of both human and bovine types. These organisms were all destroyed by biorization. Milk normally infected with tubercle bacillus from a cow with udder tuberculosis was freed by biorization from organisms toxic to guinea pigs. Not all the lactic acid and mastitis streptococci were killed by the biorization temp. (75°). However, the lactic acid organisms remaining in milk lost some of their capacity to grow at room temp., and the milk, therefore, did not sour at the normal time. A bibliography of 25 titles is appended.

H. G.

**Corn oil successful substitute for ghee.** A. E. SOUTHARD. U. S. Dept. Com. Bur. Foreign and Dom. Com., *Com. Repts.* 1920, No. 115, 946-7; *Expt. Sta. Record* 43, 563.—S. reports that American corn oil has been introduced to the trade of the Aden-Red Sea com. district of Arabia as a substitute for ghee, or clarified butter. The corn oil is said to be similar in taste and flavor to the ordinary ghee and to offer promising possibilities as a substitute.

H. G.

**Yeasts and molds in butter and cream.** T. H. LUND. *Rept. Proc. Dominion Dairy Conf. Ottawa 1918*, 59-63; *N. Y. Produce Rev. and Amer. Cream.* 48, No. 6,



282, 284, 286(1919); *Expt. Sta. Record* 42, 674.—Results of studies on the influence of pasteurization of cream on the nonbacterial flora of butter are briefly reported. Seven com. samples of creamery butter from raw cream and four from cream imperfectly pasteurized by the flash method (at temps. of 120 to 130° F.) gave an av. mold count of 2,039 per cc., and an av. yeast count of 1,700. The highest mold count occurred among the samples from beaten cream. Ten samples from pasteurized cream gave an av. mold count of 15 (with a max. of 110), and an av. yeast count (excluding one abnormally high count) of 1,182. In tests under exptl. conditions *Oidium lactis* spores in cream were completely destroyed by holding at 130° F. for 30 min. or at 135° F. for 10 mins. The yeast cells were less readily killed, a temp. of 145° F. for 30 min. being found necessary. L. suggests the use of mold and yeast counts as official tests of detg. whether butter has been made from raw or pasteurized cream. H. G.

The deterioration of butter through the agency of *Oidium lactis*. H. M. NICHOLLS. *Agr. and Stock Dept. Tasmania, Bull.* 86, 4(1919); *Expt. Sta. Record* 42, 6674.—It is stated that *Oidium* is widely prevalent in Tasmania and is the cause of much loss to creameries. Pasteurization by the holding rather than the flash method is advocated as a control measure, for N. found that the mold survives brief exposure to temps. of 170° F. and higher. He also found that the mold would grow in soft butter (butter with high moisture content or improperly refrigerated), and suggests that the non-development of spores in butter observed by Combs and Eckles (*C. A.* 12, 1571) was due to the hardness of the medium. H. G.

The detection of cocolin in butter. RAOUL MEURICE. *Ann. chim. anal. chim. appl.* 3, 143-5(1921).—The adulteration of butter with cocolin (hydrogenated coconut oil) is usually detected by the content of insol. fatty acids but there are other characteristics of the adulterant which can be utilized. It is known that the principal acids present in cocolin are lauric and myristic instead of the oleic, palmitic and stearic acids, which are commonly found in fats. 2 methods of procedure are suggested. (1) Det. the Reichert-Meissl, saponification and Hehner nos. in the usual way but express the results in cc. *N* NaOH required for 100 g. of fat. This can be done by multiplying the usual Meissl no. by 2, the saponification no. by 1.78 and the Hehner no. by 3.71. Designating these values by *M*, *S*, and *H*, a differential coeff. is obtained thus, (*M* + *H*)

—*S* =  $\Delta$ . Then for butter  $\frac{\Delta}{M}$  is a practically const. ratio (0.37-0.49). For cocolin

the ratio is about 7.4 so that adulteration is indicated if the value of the ratio is over 0.5. (2) Separate the insol. fatty acids precisely as if the Hehner no. were to be detd. Instead of weighing the acids, titrate the alc. soln. with alkali expressing the results in cc. of alkali required for 100 g. of fat. With cocolin (also called coconut stearin) the value thus obtained is about 417, whereas butter gives a value less than 341. This factor may be called *F*. Furthermore, the ratio of insol. volatile acids to sol. volatile acids does not exceed 0.156 in pure butter but with cacao butter the ratio is about 2.5. This ratio may be called *R*. By multiplying *F* × *R* the product is 53.2 for pure butter and 1042 for cocolin. By adding 5% of cocolin to pure butter the value of *F* was found to be 342.5 and of *R* × *F* to be 50. Here the adulteration was shown only by the value of *F*. With 10% cocolin, the value of *F* was 346 and of *R* × *F* was 59. W. T. HALL

The two types of Gouda cheese and Edam cheese. L. FUNDER. *Stat. Meieriforsk. Beret.* 8, 32(1919); *Mælkeritid* 32, 607-13, 627-35; *Molk. Ztg. Berlin* 29, No. 46, 267-9; *Expt. Sta. Record* 44, 75.—This is a study of the large-holed and small-holed types in relation to their chem. compn., the acidity developed, and the details of manuf. It was found that the production of large holes is due not only to the formation of gas, but to the increased moisture content characteristic of the large-holed type. H. G.

Biochemical studies on certain molds of the genus *Penicillium* important in cheese



**making.** J. DVORÁK. *Rozprawy české Akad. Cisare Frant. Josefa pro Vedy, Slovesnost a Umeni, Class II*, 26, No. 31(1917); *Expt. Sta. Record* 44, 575-6.—Three species of molds, *P. roqueforti*, *P. album*, and *P. candidum*, were cultivated either in sterilized milk or in nutrient solns. having the same mineral constituents as milk. When casein alone was added to the inorg. solns. it was strongly peptonized by the molds with the evolution of  $\text{NH}_3$ , and when both casein and lactose were added unstable acids were formed. With the addition of casein and lactic acid to the medium a small amt. of acid was developed and considerable amts. of  $\text{NH}_3$ . When lactic acid bacteria were grown in the casein-lactose cultures of the molds there was a marked decompn. of casein but only a little acid production, while *P. roqueforti* cultures gave off the typical odor of Roquefort cheese. Cultures in sterilized milk behaved like those in the casein-lactose medium, but with the production of the characteristic aroma in the case of *P. roqueforti*. Mixed cultures of *P. album* and *P. candidum* in the presence of lactic acid bacteria produced the changes in casein which occur in the ripening of Camembert, Brie, and Neufchâtel cheese. In the presence of lactic acid bacteria *P. roqueforti* produced the changes corresponding to the ripening of Roquefort cheese without the assistance of other molds, and in the absence of bacteria it retained the capacity of splitting the milk fats into fatty acids with the production of the typical aroma. These observations on *P. roqueforti* are considered contrary to some of the results of Jensen (*Landw.-Jahrb. Schweiz*, 18, No. 8, 319-405(1904); *Ann. Arg. Suisse*, 5, No. 7, 229-326(1904)), who ascribed the aroma production to a symbiosis between *P. roqueforti* and *Oidium lactis*. Some of the factors influencing the growth of the molds were also studied. In a 3% casein suspension the optimum concn. of lactic acid for the growth of *P. candidum* was 0.5%, and growth ceased in a 4.5% soln. In the case of *P. album* the optimum concn. was 1%, and growth ceased at 4%. *P. roqueforti* grew best in a 2% lactic acid soln., but did not cease growing until the concn. reached 7.5%. The presence of lactic acid bacteria reduced the assimilation of protein markedly, but increased the fat and ash content of the mycelia.

H. C.

**The relation of hydrogen-ion concentration to the heat coagulation of proteins in Swiss cheese whey.** YUZURU OKUDA AND HARPER F. ZOLLER. *J. Ind. Eng. Chem.* 13, 515-9(1921).—The optimum reaction for the heat coagulation of the proteins from cheese (Swiss) whey is about  $pH$  4.5 as determined with the hydrogen electrode. When whey is acidulated with any of the acids investigated ( $\text{HCl}$ ,  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{HC}_3\text{H}_5\text{O}_3$ ) to  $pH$  4.5 and then heated at  $98^\circ$  for 15 min. about 57% of the total nitrogen of the whey is removed in the curd. Of the remaining 43% in the whey 84% is non-albuminoid nitrogen. The important bearing of these data upon the prepn. of protein-free milk is pointed out. The conduct of methyl red in whey, before and after heating, is emphasized.

H. F. Z.

**Precipitation of grain curd casein from pasteurized milk, etc.** HARPER F. ZOLLER. *J. Ind. Eng. Chem.* 13, 510-4(1921).—It is possible to ppt. casein from pasteurized milk in granular condition (cf. *C. A.* 15, 611) with dil.  $\text{HCl}$  suitable for tray washing when the temp. of the milk is raised above the temp.,  $34^\circ$ , which was found satisfactory for unheated skim milk. The optimum pptg. temp. for the production of a granular working curd will be higher the greater the degree of pasteurization. The hydrogen ion retrogrades rapidly in the wash water bathing the curd, and this is believed to be due to the dissolving of engulfed pptd. alkaline earth phosphates from the curd grains, since the pasteurization of milk has been shown to increase materially the insol. Ca salts. Heat has a marked effect upon the texture and physical nature of the casein, so that in pasteurized milks the casein becomes denatured to the extent that it imbibes more water, the curd formed at the iso-electric point is short or brittle, and its alkali solns. are rendered more viscous.

H. F. Z.



**Does the fat influence the water content of cheese?** J. J. O. DE VRIES. *Verslag Ver. Exploit. Proefsuivelboerderij Hoorn* 1917, 30-3; *Zentr. Agr. Chem.* 49, No. 2, 80 (1920); *Expt. Sta. Record* 44, 75.—Analyses of cheeses are presented, indicating that when conditions are comparable the ratio of casein to moisture is lower in whole-milk cheese than in skim-milk cheese.

H. G.

**Feeds and their use: Inspection and analyses.** J. D. TURNER, H. D. SPEARS AND A. M. PETER. *Kentucky Sta. Bull.* 223, 71-255 (1919); *Expt. Sta. Record* 43, 373.—The protein, fat, and fiber contents of samples of the following materials are reported: Meat scrap, tankage, alfalfa meal, brewers' dried grain, distillers' dried grain, barley feed, barley mixed feed, coconut oil meal, dried beef pulp, shelled corn, corn chop, corn bran, corn feed meal, corn gluten feed, hominy feed, cottonseed meal (choice, prime, and good), cottonseed feed, linseed meal, rice bran, rye middlings, rye mixed feed, wheat bran, shorts, and middlings (with or without screenings), wheat mixed feed, red dog, and a variety of compounded grain feeds, proprietary stock feeds, calf meals, and poultry feeds. Definitions of feeding stuffs and tables of av. analyses derived from various sources are included.

H. G.

**Analyses of feeding stuffs.** M. O. JOHNSON AND K. A. CHING. *Hawaii Sta. Rept.* 1919, 42, 43.—A table is presented giving the proximate compn. of pigeon pea feed, coconut meal, alfalfa meal, Mung bean (*Phaseolus radiatus*) cane top meal, Brazilian velvet bean feed, sisal stump, and fibers from the pineapple plant and from the stump after starch extn.

H. G.

**Hydrolyzed wood meal and its utilization.** ELLENBERGER. *Illus. Landw. Ztg.* 39, No. 9-10, 33, 34 (1919); *Expt. Sta. Record* 44, 71.—E. reviews some of the previous work on the use of hydrolyzed cellulose as a feeding stuff, and reports some expts. with work horses which indicate that hydrolyzed wood meal may not only be substituted for the hay of the ration but may also replace the oats if some supplemental protein is furnished.

H. G.

**Food value of couch-grass.** M. WEIBULL. *Landmannen Tidskrift* Landman 1, 281 (1918); *Bull. Agr. Intelligence* 10, 935-6.—Dried crushed couch-grass showed on analysis protein 8.3, fat 1.2, N-free ext. 6.2, cellulose 16.5, ash 5, and H<sub>2</sub>O 7%. Its nutritive value as cattle food equals that of hay with smaller cellulose content. It contains the same glucoside, coniferin, as oats. It is especially suitable for horses and sheep.

H. A. LEPPER

**Studies on the digestibility of sunflower silage.** W. E. JOSEPH AND M. J. BLISH. *Montana Sta. Bull.* 134, 8 (1920); *Expt. Sta. Record* 43, 770-1.—Digestion trials were made with 3 steers during three 20-day periods. Clover hay alone was fed during the first period, clover hay and sunflower silage (1:3) in the second, and sunflower silage alone in the third. The silage was made from Mammoth Russian sunflowers harvested at the time 20% of the plants were in bloom. The table following summarizes the results.

*Compn. and digestibility of clover hay and sunflower silage fed to steers.*

Period.	Feed.	Compn. (dry basis)				Digestibility					
		Crude protein %	Fiber ext. %	Crude fiber %	N-free ext. %	Ash %	Dry matter %	Crude protein %	Fiber ext. %	Crude fiber %	N-free ext. %
1	Clover hay.....	13.77	1.68	31.70	47.89	4.95	60.65	63.28	37.75	51.79	71.86
2	Clover hay.....	13.19	1.65	30.65	47.76	6.73	63.23	60.72	46.49	50.73	73.14
3	Sunflower silage.....	9.60	2.47	30.67	48.65	8.60	60.35	55.23	77.62	40.81	71.48
2	Sunflower silage.....	9.82	2.40	32.66	48.69	6.41	57.27	59.88	70.63	42.16	69.75

It is concluded that the digestibility of the sunflower silage is approx. the same whether fed alone or in conjunction with clover hay, and that the coeffs. of digestibility of sunflower silage resemble those of silage made of immature corn.

H. G.



**The feeding value of Sudan grass.** G. G. ST. CLAIR POTTS. *Agr. Gas. N. S. Wales* 30, No. 9, 657-8(1919); *Expt. Sta. Record* 42, 866.—P. gives chemical analyses of Sudan grass (at four stages of maturity) and Japanese millet made by F. B. Guthrie, and cites a practical test indicating the superiority of Sudan grass over *Paspalum dilatatum* as a pasture grass for milch cows.

H. G.

**The digestibility of berseem (*Trifolium alexandrinum*).** J. A. PRESCOTT. *Sultan. Agr. Soc., Tech. Sec., Bull.* 5, 10 pp.(1920); *Expt. Sta. Record* 44, 567-8.—P. reports proximate analyses of two varieties of berseem (Egyptian clover) cut at different stages of growth, and digestion trials with sheep fed the fresh-cut forage. The third cutting of early sown Fahl berseem contained 17.2% dry matter, and the single cutting of a late sowing of this variety contained 27.2%. On the dry basis the former contained 16.83% crude protein, 3.96% ether ext., 21.83 crude fiber, and 11% ash, and the latter 15.25% crude protein, 3.2% ether ext., 24.5 crude fiber, and 8.23% ash. Misqawi berseem contained 15.3% dry matter at the first cutting (January 2) and 24.3 at the fourth (May 21). Between these dates the crude protein content on the dry basis had decreased from 19.9 to 15.65% and the ether ext. from 3.98 to 3.22%, while the crude fiber had increased from 18.1 to 23.5% and the ash remained with fair constancy at 13%. The following table summarizes the digestion trials:

*Digestibility coefficients for berseem fed to sheep.*

Variety fed.	Total org. matter %	Crude protein %	Ether ext. %	Crude fiber %	N-free ext. %
Fahl berseem—early sown . . . .	68.1	74.8	59.0	45.6	76.9
Fahl berseem—late sown . . . .	63.7	67.6	55.2	47.0	71.3
Misqawi berseem (av. of 7 trials). . .	69.4	73.0	49.9	60.5	74.0

A note on the amt of mineral matter removed from the soil by a crop of berseem is appended.

H. G.

**The causes of loss in bottles during pasteurization and sterilization (BITTING) 19.** Composition of the oil and meal from seeds of sweet pepper (COMANDUCCI, TOMASINI) 27. The biochemistry of tobacco. II. Tobacco seeds (press-cake) (PARIS) 11D. The solubility of raw cellulose in ammoniacal copper hydroxide and the utilization of this solubility for the valuation of feeding stuffs (MACH) 23.

**Food from embryo of rice.** SHIN SAWAMURA. Japan 36,720, July 6, 1920. The embryo of rice gave the following analytical results: H<sub>2</sub>O 5.73%, crude protein 24.30%, crude fat 20.12%, lecithin 0.93%, sugars 10.79%, starch 14.89%, crude fiber 9.77% and ash 13.47%. It contained a large quantity of vitamin. By treating with 0.2% NaOH, the protein and fat, etc. in the embryo go into the soln.; while by 0.1% HCl, Ca phosphate, vitamin, etc. are obtained in the soln. The two solns. are mixed together and a small quantity of lime water is added. The ppt. thus obtained is collected, washed with H<sub>2</sub>O, and dried. It contains a large quantity of vitamin and H<sub>2</sub>O 4.87, crude protein 41.55%, crude fat contg. lecithin 46.50% and ash 3.86%, P<sub>2</sub>O<sub>5</sub> 1.19%, and CaO 1.00%.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**Post-graduate training in industrial chemistry.** A. COTTRELL. *J. Soc. Chem. Ind.* 40, 215-6R(1921).

E. H.



The chemical industry and trade of Holland. O. P. HOPKINS. *J. Ind. Eng. Chem.* 13, 593-9(1921). E. H.

Economies in the handling of liquid coal-tar chemicals. S. P. MILLER. *J. Soc. Chem. Ind.* 40, 153-5T(1921).—Methods used by the Chemical Department of The Barrett Company are described. E. H.

Prevention of injury to arable land by absorption of sulfur dioxide by means of charcoal. ANON. Tech. Bureau for Chem. Ind., Wiesbaden. *Chem. Ztg.* 45, 96-7(1921).—As the industries increase, the waste gases encroach more and more upon the outlying farm and forest lands. The problem is now being solved by the absorption of  $\text{SO}_2$  by charcoal. Previous attempts to remove  $\text{SO}_2$  from gases by  $\text{H}_2\text{O}$  have been ineffective. Charcoal absorbs many more times its vol. of  $\text{SO}_2$  than  $\text{H}_2\text{O}$ , and whereas absorption by  $\text{H}_2\text{O}$  decreases rapidly with decrease in concn. of  $\text{SO}_2$ , absorption by charcoal is independent of concn. Furthermore by the use of charcoal,  $\text{SO}_2$  is economically recovered in concd. form without the inhibitive fuel expense incident to its recovery from  $\text{H}_2\text{O}$ . C. C. DAVIS

Mineral resources of the United States in 1920. G. F. LOUGHLIN AND MARTHA B. CLARK. *Separate* 123 pp. (published July 7, 1921). E. H.

Determining tank capacity or contents. W. F. SCHAPHORST. *Textile World* 60, 687(1921).—A logarithmic chart for computing gallons, pounds, tons and cu. feet of  $\text{H}_2\text{O}$  in rectangular tanks, is given. CHAS. E. MULLIN

Heat transmission by liquids and gases as a function of the velocity. H. PREUSZLER. *Stahl u. Eisen* 41, 827(1921).—The heat capacity is the determining factor in heat transmission rather than the velocity. The known formulas for heat transmission through conduction and radiation are found to be applicable to boilers and commercial heat reservoirs. R. S. DRAN

The Avrutik continuous and automatic shifting process for separating liquids and solids. JOSEPH AVRUTIK. *Louisiana Planter* 66, 379-80(1921).—A design of the app. and description of the principles involved are given. Three centrifugal baskets placed one above the other, and permitting an overflow for solids from the upper basket into the lower baskets, are the principal features of the app. The material under treatment can be washed as desired. C. H. CHRISTMAN

Requirements for ball bearing lubrication. J. B. CASTINO. *Sci. Lubrication* 1, No. 2, 18(1921).—Suggested specifications are drawn covering general characteristics. Several grades of oils are selected and their use under varying conditions of operation given. D. K. FRENCH

The flash point of lubricating oils. C. M. LARSON. *Sci. Lubrication* 1, No. 3, 14-17(1921).—A discussion of the flash test including a history of its development. Too much reliance must not be given to the results obtained as they are frequently a false index to the distn. range and evapn. rates of oils tested. D. K. FRENCH

Chemistry of oil. W. F. PARISH. *Sci. Lubrication* 1, No. 3, 30-33(1921).—Relates to the development of various oil testing methods from 450 B. C. to date. D. K. FRENCH

Lubrication of air compressors. ANON. *Proc. Comp. Air Soc.; Sci. Lubrication* 1, No. 4, 11-13(1921).—The important requirements of air compressor lubricants are proper body and freedom of a tendency to carbouize; the latter is covered by several considerations. Tentative recommendations as to proper physical tests for both paraffin and asphalt base oils for use are given. The quantity of oil to feed is also discussed. D. K. FRENCH

Mineral oil versus castor oil for the lubrication of internal-combustion engines. WM. F. PARISH. *Sci. Lubrication* 1, 7(1921).—Mineral oil is almost universally used in the U. S., castor oil very generally on the continent and in the United Kingdom.



During the war the use by the various flying services of both American and foreign built planes resulted in an investigation to det. the relative merits of the two types of oil. Castor oil, a heavy blend similar to mineral castor and Liberty Aero oil were used; 18 motors in three groups of six were first subjected to a 4-hour block test and then one engine from each group was placed in a plane for a 30-hour flying test. Castor oil produced heavy shellac-like carbon deposits, the mineral oils light flaky, easily removed deposits. The engines ran more easily on Liberty Aero oil. Castor oil, contrary to the generally accepted belief, absorbed gasoline and became much lighter while the mineral oils did not. The condition of the engines using Liberty Aero oil was much the best, and the results of the tests were that mineral oils were established as the most satisfactory lubricants. Castor oil wears out rapidly whereas mineral oils do not. The cost of castor oil was over three times that of Liberty Aero oil. Complete tables of all tests are given.

D. K. FRENCH

KRAIS, PAUL: *Werkstoffe*. Handwörterbuch der technischen Waren und ihrer Bestandteile. Leipzig: Verlag von Johann Ambrosius Barth. 541 pp. M 115. For review see *Tonind Ztg.* 45, 645(1921).

#### 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

Mineral waters. G. ISSOGLIO. *Ann. chim. sci. ind.* 37, 83(1921).—Review of analytical data.

E. FIERTZ

The presence of vanadium and arsenic in the water from some wells in the city of Buenos Aires. ATILIO A. BADO AND ALBERTO J. ZANETTA. *Anales asoc. quim. Argentina* 9, 24-5(1921).—Traces of As and V compts. were found in the water from a number of deep wells.

L. E. GILSON

Investigations of the Elbe River water at Magdeburg and Hamburg. OTTO WENDEL. *Z. angew. Chem.* 33, Aufsatzteil, 82-4, 89-92(1920); cf. *C. A.* 15, 2320.—Sanitary analyses of the Elbe waters are given, weekly and monthly for 1919, and yearly from 1912 to 1919 inclusive. Mineral content varies according to time and place of sampling.

W. U. GALLAHER

The treatment of boiler feed water. FERD. BLUMENTHAL. *Z. angew. Chem.* 34, Aufsatzteil, 189-92(1921).—B. criticizes article by Pren (*C. A.* 15, 2321) on the same subject. Treatment of boiler feed water by lime-soda,  $\text{BaCO}_3$ , and  $\text{NaOH}$  is discussed. Regenerative preheating to  $40^\circ$  may not reduce the amt. of chemical necessary for softening of the feed water.

W. U. GALLAHER

Boiler scale, its prevention and removal. W. HACKER. *Glasind.* 31, 417-20(1920).

J. B. PATCH

Rusting of steam boilers (BRUHNS) 9. The cause of corrosion of steam boilers (PARIS) 9. Zero water in wool dyeing (TIGER) 25.

#### 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER AND ALBERT R. MERRZ

Chemical fertilizers. G. R. P. D'UTRA. *Adubos chimicos*. Sao Paulo: *Soc. Agr. Com. e Obras Pub. Estado, Sao Paulo* 1920, pp 205; *Expt. Sta. Record* 44, 128. This publication deals with the origin, compn., manuf., and use of chem. fertilizers with particular reference to agricultural conditions and crops in the State of Sao Paulo.



Information is also given on the selection and purchase of fertilizers on the basis of their compn.

H. G.

**Chemical fertilizers in Italian agriculture.** BORGHESE. *Vie agr. et rurale* 9, No. 27, 14-9(1920); *Expt. Sta. Record* 43, 728.—A general review is given of the fertilizer resources of Italy and of the consumption and practical use of different types.  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{CaCN}_2$  are the three most important nitrogenous fertilizers used. Superphosphate and Thomas slag are the most important phosphatic fertilizers, although some bone meal and guano are used. It is stated that an immense reserve of potash exists in Italy in the different natural resources, of which the mineral leucite is considered to be an important source.

H. G.

**Danish experiments with different nitrogenous fertilizers in the years 1914-1918.** JACOBSEN. *Deut. Landw. Presse* 47, 95-6, 121-22, 130-31(1920); *Expt. Sta. Record* 44, 128.—Comparative tests of Chilean, Norwegian, and  $\text{NH}_4$  nitrates,  $(\text{NH}_4)_2\text{SO}_4$ , and lime N from German, Swedish, and Norwegian sources are reported, barley, oats, orchard grass, beets and potatoes being used as crops. In addition, mixts. of Chilean nitrate with  $(\text{NH}_4)_2\text{SO}_4$  and with lime N were also tested. In the 4 years 276 tests were conducted. Chilean and Norwegian nitrates gave the best results, especially with barley and oats, the results being about equal.  $\text{NH}_4\text{NO}_3$  was second in effectiveness, followed closely in their order by the  $(\text{NH}_4)_2\text{SO}_4$  and lime N. The effectiveness of the different fertilizers varied with the kind of soil and its reaction. The residual effect of all the fertilizers was generally small. The fertilizers exerted a slightly depressing influence on the dry-matter content of beets, which was less for lime N than for Chilean nitrate. The dry-matter content of potatoes was more depressed by lime N than by Chilean nitrate, however.  $\text{NH}_4\text{NO}_3$  gave better results when broadcast in early spring before planting than at the time of planting. The opposite was true with Chilean nitrate. The mixts. of Chilean nitrate with  $(\text{NH}_4)_2\text{SO}_4$  and with lime N gave results equal to the av. of those given by the individual fertilizers in each mixt.

H. G.

**Tests of organic and pepto-humic fertilizers.** J. AUROUSSEAU. *Tech. Engrais* 1, No. 1, 9-11(1920); *Expt. Sta. Record* 44, 420.—Comparative tests of a so-called pepto-humic fertilizer, consisting of a combination of a peptonized fertilizer of animal origin and a humus fertilizer with a peat base, with complete mineral fertilizers and complete fertilizers with an org. base are reported. It was found that on fertile soil this fertilizer gave better results than the other fertilizers with beets, carrots, potatoes, beans, oats, and prairie hay. It is said to contain 6% of N, 6% of phosphoric acid, and 4% of potash. The superior activity of this fertilizer is attributed to the active components of its so-called black matter or colloid content.

H. G.

**Humogen experiments.** S. N. SILL. *Bihar Orissa Agr. Dept., Expt. Farms Sci. Sects. Repts.* 1919, 19; *Expt. Sta. Record* 44, 128.—Expts. with humogen on maize to det. its fertilizing action in comparison with that of such readily available org. fertilizers as cattle manure and green manure showed that in a 1-year trial the humogen had very little effect in increasing crop production.

H. G.

**The fertilizing action of Peruvian bark residue.** O. NOLTE. *Deut. Landw. Presse* 47, 262(1920); *Expt. Sta. Record* 44, 25.—Pot and field expts. with mustard on light sandy soil to test the value of Peruvian bark residue as a source of N showed that this residue gave no evidence of having any fertilizing value.

H. G.

**Investigation on the action of guanol.** D. MEYER AND K. SCHROTER. *Blätter Zuckerrüb.* 27, 90-5(1920); *Expt. Sta. Record* 44, 25.—In a study of the fertilizing action of guanol, pot expts. with mustard on sandy loam soil, and field expts. with potatoes on loamy sand soil and with sugar beets on heavy loam soil are reported. In the pot expts. with mustard better results were obtained when guanol was used with than without stable manure. In the former case the action was relatively small, being



only about 68.2% of that of  $\text{NH}_4\text{NO}_3$ . The potato crop was increased somewhat in the field expts., but there was very little favorable action of the guanol evident on sugar beets. Further expts. are deemed necessary. H. G.

**Determination of cyanamide and dicyandiamide in calcium cyanamide.** MARQUEVROL, P. LORIETTE, AND L. DESVERGNES. *Ann. chim. anal.* [2] 2, 164-7 (1920); *Expt. Sta. Record* 43, 804.—The authors present evidence, both from the literature and from lab. investigation of different methods, indicating that the original methods of Caro for detg. cyanamide and dicyandiamide in  $\text{CaCN}_2$  (*C. A.* 6, 131) are more accurate than later modifications of other authors. In particular, volumetric methods, such as that of Kappen (*C. A.* 3, 2483), based upon the detn. of the Ag in Ag cyanamide and dicyandiamide are considered to be inexact. H. G.

**Experiments with sodium chloride and potassium salts.** H. R. CHRISTENSEN. *Tidsskr. Planteavl* 26, No. 5, 737-823 (1920); *Expt. Sta. Record* 43, 630; cf. *C. A.* 15, 1959.—The results of the works of others bearing on the subject are briefly reviewed, and expts. conducted at the Danish state expt. stations on the fertilizing influence of NaCl and K salts on such root crops as mangolds, swedes, and potatoes, are reported. The results indicate that under certain conditions NaCl has a very stimulating effect on the production of dry matter in crops, but this was evident only in the case of mangolds for Danish crops. Raw Stassfurt salts, kainite for instance, consistently replaced NaCl in this respect. It is concluded that the more extensive use of low-grade potash salts is justified and also the use of NaCl. It is the opinion that the use of these salts, NaCl in particular, tends to offset the injurious effect of summer droughts on the growth of mangolds. NaCl as a rule had no effect on swedes, and there was no difference between the results obtained with high- and low-grade potash fertilizers. High-grade potash salts were preferable for potatoes, however. Kainite and NaCl often had a directly negative influence upon potatoes, as indicated by small production and low quality. H. G.

**Ammonium nitrate.** L. MALPEAUX. *Vie agr. et rurale* 9, No. 17, 294-6 (1920); *Expt. Sta. Record* 43, 427.—M. briefly reviews the results of work by himself and others on the use of  $\text{NH}_4\text{NO}_3$  as a fertilizer, and draws conclusions as to its practical use. His experience demonstrated that the nitric N of  $\text{NH}_4\text{NO}_3$  is as effective as that of  $\text{NaNO}_3$ , and its ammoniacal N is as effective as that of  $(\text{NH}_4)_2\text{SO}_4$ . With certain crops, such as beets, it was found that the use of  $\text{NH}_4\text{NO}_3$  gave results similar to those obtained when using a mixt. of  $\text{NaNO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ .  $\text{NH}_4\text{NO}_3$  had a regular and sufficiently prolonged action on crops, and possessed the advantage of introducing no Na into the soil. It is noted that the proper use of  $\text{NH}_4\text{NO}_3$  varies with the crop and the soil. H. G.

**Ammonium sulfate nitrate, a new German nitrogenous fertilizer.** *Blätter Zuckererz.* 27, 82-83 (1920); *Expt. Sta. Record* 44, 216.— $\text{NH}_4$  sulfate nitrate contains 27% of N, 19% as  $\text{NH}_4$ , and about 8% as nitrate. H. G.

**The effects of nitrate of soda on soils.** W. P. KELLEY. *Calif. Sta. Rept.* 1919, 14; *Expt. Sta. Record* 42, 814.—After  $\text{NaNO}_3$  was used annually for a period of 11 years on citrus trees the trees became wholly unprofitable and showed the most extreme symptoms of mottle-leaf. Soil studies showed that at first Ca was set free by  $\text{NaNO}_3$ , producing beneficial effects. In course of time the available Ca became reduced to a low point, and further applications of  $\text{NaNO}_3$  brought about excessive concns. of sol. Na in the soil soln. Concurrently, the soil became greatly deflocculated and impervious. H. G.

**Action of lime on acid humiferous soil.** S. OJÉN. *Medd. Stat. Skogsforsöksanst.* 1916-17, No. 13-14, pt. 2, 1287-1301; *Intern. Inst. Agr. (Rome)*, *Intern. Rev. Sci. and Pract. Agr.* 10, No. 4, 393-4 (1919); *Expt. Sta. Record* 43, 325.—Investigations con-



ducted in Sweden are reported from which it is believed that vegetation is not injured in soils by free humic acids but that the acid character of unlimed humiferous soil is due to absorbed org. acids. The xerophytic growth of peat-bog plants is attributed to lack of O for the roots; accumulation of injurious excreta, such as oxalic and formic acids; and fixation of nutrient elements by humus and the consequent formation of mycorrhiza as a form of adaptation to the lack of nitrates. It is further pointed out that the different conditions found in unsubmerged peat bogs are modified by liming, as the formation of Ca humate not only neutralizes the acid toxic substances but also sets free the fertilizing elements absorbed. On the other hand it is stated that Ca humates oxidize more easily than the corresponding humic acids. Liming on these soils had no influence on the water supply of plants. H. G.

**The question of lime fertilization.** P. LIECHTI AND E. TRUNINGER. *Landw. Jahrb. Schweiz* 32, 573-88(1918); *Zentr. Agr. Chem.* 49, 13-6(1920); *Expt. Sta. Record* 43, 325.—In a second contribution to the subject (*Landw. Jahrb. Schweiz* 30, 480-8(1916)), pot culture expts. with oats, red clover, and carrots on acid soil deficient in lime are reported, to det. the influence of the fineness and amt. of lime.  $\text{CaCO}_3$  of 5 different degrees of fineness was used, having grain sizes of from less than 0.11 to 2 mm., and was added in aunts. varying from 1000 to 8000 kg. per hectare (890 to 7,120 lbs. per acre). It was found that degree of fineness and amt. of application of lime had only a slight influence in the case of oats. The coarse-grained lime in relatively large additions had a favorable influence on red clover and carrots, while the fine-grained lime had an injurious effect, especially on carrots. The depressing influence of fine-grained lime on the action of bone meal  $\text{H}_2\text{PO}_4$  decreased as the lime grains increased in size. Lime of 3 mm. size had no depressing influence. The influence of lime on the action of superphosphate  $\text{P}_2\text{O}_5$  was detd. more by the physiol. behavior of the test crop than by the degree of fineness of the lime. Fine- and coarse-grained lime had about the same favorable influence on the nitrification of  $(\text{NH}_4)_2\text{SO}_4$ . H. G.

**Inoculation of legumes with nitragin.** ANON. *Rev. Assoc. Rural Uruguay* 48, No. 12, 781-4(1919); *Expt. Sta. Record* 43, 217.—This report summarizes the works of others bearing on the subject and deals with experience which indicates that nitragin is not applicable to all soils, especially those in poor tilth and those rich in N. It is concluded that the proper soil conditions under which nitragin may be effectively used are poverty in N, sufficiency of other fertility constituents, and moisture, and the soil neither acid nor excessively alk. H. G.

**Nitrogen bacteria fertilizers.** NOLTE. *Z. Landw. Kammer Braunschweig* 88, 437-8(1919); *Expt. Sta. Record* 43, 221.—Lab. tests of three so-called N bacteria fertilizers, using a nutritive salt soln., are reported. It was found that two of the fertilizers contained free living N organisms which, however, were able to fix only small quantities of N under favorable conditions. A cropping expt. with oats and mustard on sand soil using the bacteria fertilizers with and without  $(\text{NH}_4)_2\text{SO}_4$  showed no marked action on the part of the bacteria fertilizers to indicate their value as sources of N. H. G.

**Relative efficiency of different carriers of nitrogenous materials.** C. B. WILLIAMS. *N. Carolina Sta. Rept.* 1919, 28-7; *Expt. Sta. Record* 43, 427.—The av. results of field expts. by the station are said to show that with regard to relative fertilizing value, the different common nitrogenous fertilizers stand in the following order:  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CaCN}_2$ , dried blood, and cottonseed meal for cotton; and  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CaCN}_2$ , cottonseed meal, and dried blood for corn. H. G.

**Sulfur in plants and soils.** A. M. PETER. *Kentucky Sta. Rept.* 1918, Pt. 1, 38-9; *Expt. Sta. Record* 43, 324-5.—Expts. on the composting of S with soil, phosphate



rock, and manure, using soil from the station farm, showed that nearly three-fourths of the phosphate added or already present in the soil was finally rendered sol. in  $\text{NH}_4$  citrate soln., although the action was slow in beginning and did not progress properly until after the addition of sulfolysing organisms. These expts. are considered to indicate the practicability of this method for producing acid phosphate on the farm. Lab. expts. with 8 Kentucky soils of different types showed that S added at the rate of 500 parts to the million of soil was nearly all converted into sulfate in a month. There was little difference in the sulfolysing power of the several soils, none of them exceeding the station farm soil in this property. H. G.

**Soils.** C. S. TAYLOR. *Bihar Orissa Agr. Dept., Expt. Farms Sci. Sects. Repts.* 1919, 1-3; *Expt. Sta. Record* 44, 128-9.—Expts. on the effect of phosphatic fertilizers with and without green manure on poor rice soils showed that the phosphates by themselves had no influence on the ultimate crop, while the more active phosphates in combination with green manure had a marked effect on the crop when applied at the right time. It was found to be essential in such poor soil to manure with phosphoric acid before sowing the green manure. Apatite had no effect greater than the assumed limits of exptl. error. H. G.

**The value of raw phosphate in agriculture.** W. V. KNISRIEM. *Deut. Landw. Presse* 47, 345-6(1920); *Expt. Sta. Record* 43, 817.—K. reviews a number of expts. on the fertilizing value of raw rock phosphate on different soils with different crops. It was found that phosphorite meal showed practically no fertilizing action on lowland moor soil rich in basic matter, except in cases where free sulfates existed which acted on the phosphorite. It is concluded that raw phosphate can be used to advantage only on upland moor soils, and then only after it has been composted with sulfates and peat litter or smelted with lime, sand, and soda. H. G.

**I. The relative availability of acid phosphate and the native soil phosphates in the presence of pulverized limestone. II. Future of the agricultural lime industry.** J. L. BURGESS. *N. C. Dept. Agr. Bull.* 41, No. 3, 24(1920); *Expt. Sta. Record* 43, 26-7. In Part I of this bulletin a review and summary of a number of works by others on the availability of acid and native phosphate in the presence of lime are given, from which the conclusion is drawn that while acid phosphate reverts to insol. forms in the soil, those forms to which it reverts in the presence of lime are relatively less insol. and more available than those to which it reverts in the presence of Fe and Al compds. It is therefore recommended that pulverized limestone be mixed with acid phosphate to prevent the formation of insol. phosphates of Fe and Al in the soil. Part II is an address on the future of the agricultural lime industry. H. G.

**Phosphoric acid utilization, with special reference to conditions in Bavaria.** H. FISCHER. *Landw. Jahrb. Bayern* 9, 161-9(1919); *Expt. Sta. Record* 43, 629-30.—F. reviews a number of studies by himself and others on the ways in which  $\text{P}_2\text{O}_5$  is placed in available condition in soils, particularly those of Bavaria. He takes up especially the unlocking of soil phosphates by soil acids, chem. action and mass action of soil amendments, and heat and soil bacteria. With reference to the action of soil amendments, it is believed that liming has a favorable effect upon the soly. of soil phosphates owing to its pptg. action on solns. of Fe salts. This is thought to explain the relatively large amts. of available P in certain of the Bavarian soils which are rich in lime. It is also concluded that the action of heat and soil bacteria on the production of  $\text{CO}_2$  in soils has a marked effect upon the availability of soil phosphates, and the use of org. matter as an aid in this action is therefore recommended. H. G.

**Phosphatic slags.** J. VANDORMAEL. *J. Soc. Natl. Agr. Belg.* 2, 92-3(1920); *Expt. Sta. Record* 43, 127.—Analyses of different phosphatic slags are reported and briefly discussed, to show that, aside from the basic Ca phosphate, phosphatic



slags contain not only elements such as P, Ca, and Si, which are normally necessary in the construction of plant tissues, but also diastatic elements such as Mn and S in sol. form.

H. G.

**New guano deposits in the Island of Sardinia.** A. DE DOMINICIS. *Ann. scuola agr. Portici* 15, 12(1919); *Bull. Agr. Intelligence* 11, 296.—Altara discovered 6 caves containing important deposits of bat guano in the districts of Dorgoli, Oliena and Orosei. D. states that the chem. nature of this guano is of the two types, the nitrogenous, and the phosphatic guano, and that though it contains much foreign matter it is a rich fertilizer that can be readily utilized. The following are analytical results (17 samples) showing max. and minimum percentages:—Water and volatile substances at 110°: 6.20 to 25.38; org. matter 5.55 to 46.27; mineral substances 30.23 to 75.87; total N 44 to 7.14; nitric N 12 to 3.91; uric N 17 to 4.45. The av. percentages are resp.: 15.09, 26.12, 58.77, 2.86, 1.27, and 1.56%.

H. G.

**The role and use of magnesium in fertilizers.** J. LEFÈVRE. *Vie agr. et rurale* 10, No. 6, 105-7(1920); *Expt. Sta. Record* 42, 723.—A review of the results of different expts. on the value of Mg as an element in fertilizers is given. Analyses of different crops are given showing an appreciable percentage of Mg. It is the opinion that the use of Mg in the form of dolomite is advisable, particularly for viticulture.

H. G.

**Magnesia and the fertilizing of vines.** J. LEFÈVRE. *Rev. vit.* 51, 394-8 (1919); *Expt. Sta. Record* 42, 737.—A brief summary is given of the knowledge relative to the use of Mg as a fertilizer, with special reference to its use for grapes. Special attention is called to the combination of Mg and Ca oxides which is manufactured by several factories in France and sold under the name of dolomagnesium. When the Mg is administered in this form, either alone or in combination with other fertilizers, it has none of the toxic effects of Mg sulfate and chloride. In addition to its value as a direct nutrient and in amending acid soils it has also an antichlorotic action. A number of expts. conducted under varying conditions indicate that a normal dose of dolomagnesium is from 500 to 1,000 kg. per hectare; 2,000 kg. per hectare (1,750 lbs. per acre) can be used without injury in making an initial application. Dolomagnesium can be mixed with other fertilizers except nitrogenous fertilizers.

H. G.

**How to convert sugar-cane megass into a profitable fertilizer.** K. ADINARAYANA RAO. *J. Madras Agr. Students' Union* 8, No. 7, 184-9(1920); *Expt. Sta. Record* 44, 513.—Preliminary expts. on the bacterization of sugar-cane megass for the production of an available nitrogenous fertilizer are briefly reported. Samples of the materials were dried and inoculated with *Azotobacter*, *Rhodospirillum*, and *Clostridium*. It was found that the material contained from 1.2 to 1.4% of N after being acted upon by the N-fixing organisms for two months. The decomposition of cellulose was more pronounced where pure cultures of cellulose-decomposing organisms were introduced. The expt. is being continued.

H. G.

**Investigations on the conservation of liquid manure by the addition of different materials.** O. LEMMERMANN AND H. WIESSMANN. *Landw. Jahrb.* 52, 297-341 (1918); *Expt. Sta. Record* 42, 721.—Investigations are reported on the conservation of liquid manure by the addition of different materials, especially brown coal, peat,  $H_2SO_4$ ,  $NaHSO_4$ , superphosphate, kainite, gypsum, and formalin. The brown coal used was able to combine with 5.122% of  $NH_3$ . The compd. formed was very stable at ordinary temps., but released a part of the  $NH_3$  at 100°. The addition of from 50 to 60% of air-dry brown coal containing 80% dry matter was sufficient to preserve perfectly the liquid manure used. Fertilizer expts. with liquid manure conserved with brown coal gave good results, and the N in the so-treated liquid manure was more active than an equal amt. of N in the form of  $(NH_4)_2SO_4$ . The addition of 20% of peat to liquid manure resulted in a loss of 51.03% of the N after 62 days, in spite of the fact that the



peat possessed the power to form a very stable chem. compd. with  $\text{NH}_4$ . The addition of from 1.5 to 2% of  $\text{H}_2\text{SO}_4$  of  $66^\circ \text{B}$ . protected liquid manure from N losses. The addition of 7%  $\text{NaHSO}_4$  of an acidity equiv. to 0.3501 g. of  $\text{H}_2\text{SO}_4$  per g. of the substance was sufficient to conserve the liquid manure used. The N loss after 62 days, by the addition of 10% superphosphate, was 27.48%. The use of kainite did not conserve liquid manure. An addition of 15% resulted in a loss of 70.18% of the N within 62 days. Gypsum gave somewhat better results than kainite, although by an equal addition the N loss was 63.86% within 62 days. The addition of 0.25% of formalin to fresh urine depressed fermentation of the urea. An addition of 6% formalin to liquid manure was equally effective and the N loss after 62 days was only 1.7%. Expts. with numerous other materials showed that small quantities of  $\text{ZnCl}_2$  and  $\text{CuSO}_4$  sufficed to prevent urea fermentation, while other salts, such as  $\text{NaCl}$  and  $\text{Na}_2\text{Sulfate}$ , when used in the same quantities, were unable to do so. It was found that in studies on the conservation of liquid manure it is of the greatest importance to know the exact characteristics of the liquid manure used.

H. G.

**Mechanical and chemical analyses of part of the agronomic station at La Jaille.** C. T. ALLDER. *Guadeloupe Rap. Sta. Agron.* 1, 35-7(1918-19); *Expt. Sta. Record* 43, 621.—Mechanical analyses of samples of soil from the station show a high percentage of fine sand, silt, and clay. On this basis the soils of the locality are classed as fine sandy clay. The subsoil is of the same mechanical compn. Chem. analyses show that these soils are poor in lime and other alk. materials, but contain no sol. free acids. The total contents of potash and  $\text{H}_3\text{PO}_4$  are not high, and the available content approaches the minimum permissible. There is a 3% content of org. matter, and the N content is also high.

H. G.

**Analyses of soils of Eritrea.** A. CAUDA. *Agr. Colon. (Italy)* 14, 226-8 (1920); *Expt. Sta. Record* 43, 721.—Analyses of samples of a number of different soils from Eritrea are reported and discussed, showing that the matter sol. in concd.  $\text{HCl}$  varies from a minimum of 97.51 to a max. of 104.76 g. per thousand of fine soil.  $\text{CaO}$  comprised from 0.76 to 23% of the sol. matter, potash from 1.58 to 7.93%,  $\text{H}_3\text{PO}_4$  from 0.38 to 2.68%, and total N from 0.37 to 1.96%. It is concluded that the av. chem. compn. of these soils corresponds to good Italian field soils.

H. G.

**Variation of composition of adjacent soils.** G. VERNET. *Bull. Agr. Inst. Sci. Saigon (Cochin, China)* 2, 263-8(1920); *Expt. Sta. Record* 44, 213.—Analyses of 8 samples of soil taken from within a radius of 100 meters in a rice field showed marked variations in physical and chem. properties, caused by the slope and close proximity to a stream. Similar variations in physical and chem. properties were also found in other soils growing different crops.

H. G.

**The chemical and biological aspect of Bhata soil, of Chandkhuri experimental farm, Central Province.** A. R. PONMANAHIA Aiyer. *Agr. J. India* 15, 644-9(1920).—The Bhata soil contains large amts. of coarse material which is partly the cause of their infertility and failure of sann-hemp. Chem. analyses show that the soil is low in P. Growth of legumes is improved by the addition of phosphate fertilizers. Ammonification and nitrification in the soil are good.

J. J. SKINNER

**The disinfection of soil and its partial sterilization.** L. MALPRAUX. *Vie agr. et rurale* 10, No. 6, 94-7(1920); *Expt. Sta. Record* 42, 718.—A review is given of a number of expts. by others on the partial sterilization of soils, with particular reference to the use of S compds.

H. G. \*

**The care of the soil.** H. E. P. HODSOLL. *J. Roy. Hort. Soc.* 45, No. 1, 22-8 (1919); *Expt. Sta. Record* 43, 209.—A brief review is given of the mechanical, chem., and biological properties of soils, together with information as to their proper maintenance.

H. G.



**Soil making.** E. J. RUSSELL. *J. Roy. Hort. Soc.* 44, 1-12(1919); *Expt. Sta. Record* 43, 209.—The origin, compn., and treatment of normal agricultural soils are discussed, the general conclusion being drawn that the making of soil requires proper mineral matter, org. matter, and conditions suitable for the decompn. of the org. matter.

H. G.

**The soil viewed as a permanent depository of moisture.** I. R. FONTANA. *Univ. Tucumán, Ext. Agr. Bot.* 19, 1-2(1918); *Expt. Sta. Record* 43, 320.—This is a popular discussion of physical and chem. factors governing the moisture content of soils. H. G.

**Effect of initial moisture content on subsequent moisture movement in soil.** G. ROBERTS. *Kentucky Sta. Repts.* 1918, Pt. 1, 28-9; *Expt. Sta. Record* 43, 320-1.—Exptl. work in progress, dealing with moisture movement in dry and wet sand and in soils of different initial moisture contents, has shown that with sand the movement is only from 1.3 to 1.7 times as great when wet as when dry, and that with soils there is very little greater movement in soil contg. a small amt. of initial free moisture than in soil previously air dry.

H. G.

**Experiments in the reclamation of alkali soil.** F. B. HEADLEY. U. S. Dept. Agr., *Dept. Circ.* 80, pp. 16-8(1920); *Expt. Sta. Record* 43, 420; cf. C. A. 14, 1177.—A series of 2-year rotations begun in 1917 on the Newlands (formerly the Truckee-Carson) Reclamation Project Expt. Farm near Fallon, Nev. to study the effect of fertilizer in improving alkali soils have shown a gradual improvement, which is proceeding faster on soils receiving fertilizer in the rotation. Expts. begun in 1914, the treatments in which included the application of gypsum,  $H_2SO_4$ , fertilizer, tile subdrainage, and green manuring with clover, showed that the yields of the soils treated with gypsum and  $H_2SO_4$  have been decidedly greater each year than those from untreated plots, but not large enough to be profitable.

H. G.

**Reactions of experimental soils and the lime requirements of the soils of Malmöhus, Sweden.** L. FORSBERG. *Malmö. Låns. Hushåll. Sällsk. Kvitlskr.* 1919, 458-63; *Expt. Sta. Record* 43, 623.—Data on the reactions of representative sand and clay soils from the Province of Malmöhus, detd. each successive year for 11 years, showed 43% of the sand soils to be acid, 13% neutral, and 42% alk. in reaction. Of the clay soils, 30% were acid, 13% neutral, and 57% alk. These results are taken to indicate the advisability of testing all sand and clay soils for acidity, and the litmus test is recommended for this purpose. Marling of these soils, while successful, was found to be expensive, and the use of com. ground limestone is recommended for reducing the acidity.

H. G.

**The value of late glacial drift from the Province of Bohus as liming material for peat soils poor in lime.** H. VON FEILITZEN AND E. NYSTRÖM. *Svenska Mosskulturför. Tidskr.* 34, 115-24(1920); *Expt. Sta. Record* 43, 631.—Expts. are reported on peat soils poor in lime growing red clover to compare coarse and finely ground glacial drift with ground limestone as sources of lime. These materials were added in amts. equiv. to 1000, 2000, and 4000 kg. of  $CaO$  per hectare (800, 1750, and 3560 lbs. per acre). The finely ground glacial drift gave results comparable to those given by the ground limestone, and in some cases gave better results. The finely ground drift gave much better results than the coarse drift, and in the smallest applications was better than the largest applications of the coarse material. Comparisons of the solubilities of the glacial drift and of ground limestone in water satd. with  $CO_2$  made by H. Christensen showed that the coarse drift material was slowly sol. as compared to the fine drift, and that the fine drift was in all cases equal in solv. to the ground limestone. It is concluded that this glacial drift is equal to high-grade limestone as a carrier of lime, but that it must be finely ground.

H. G.

**A comparative study of cropped and virgin soils.** C. E. MILLAR. *Mich. Sta.*



*Quart. Bull.* 2, 195-6(1920); *Expt. Sta. Record* 43, 622.—An extension of expts. previously reported (*C. A.* 13, 2046) to include soils from many sections of Michigan confirms the conclusions of the previous report. Further studies to det. the nature of the material going into soln. showed a larger total residue for the virgin than for the depleted soils. A large part of this residue was volatile, and while all the exts. showed large quantities of org. matter there are considerable quantities of carbonates present in the exts. which would be decomposed on ignition. More Ca was extd. from virgin than from cropped soils. These expts. are being continued. H. G.

**The mixing of mineral soils and moor soils.** G. RITTER. *Fühling's Landw. Ztg.* 67, No. 1-2, 16-31(1918); *Expt. Sta. Record* 42, 622.—Vegetation expts. and studies are reported of nitrification and N fixation in mixts. of loamy sand soils and moor soils. The purpose is to show the advantages to either soil of such a mixt. with reference to physical and chem. condition. It was found that the addition of virgin moor soil or peat litter to a light mineral soil increased the nitrate content, also the nitrate content of an upland moor soil was increased following an intermixture of lime and good mineral soil. It is concluded that the physical, chem., and biol. properties of an upland moor soil or a light mineral soil can be improved by mixing these two soil types. H. G.

**Smoke injury in soils.** W. LEININGEN-WESTERBURG. *Centr. Gesam. Forstw.* 46, No. 5-6, 129-44(1920); *Expt. Sta. Record* 44, 509.—A number of expts. on the injurious action of industrial smoke and dust on vegetation are reported. These led to the conclusion that such injury is not simply a chem. or botanical problem, but that the effect of these materials on soils is of considerable indirect importance and should always be taken into account in such studies. H. G.

**Soils.** M. J. FUNCHESS. *Alabama Agr. Expt. Sta. Rept.* 1919, 19; *Expt. Sta. Record* 42, 815-6; cf. *C. A.* 14, 443.—Further studies at the station on the toxicity of sol. Mn in acid soils (*C. A.* 12, 2222) showed that Mn may be regarded as a very good indicator of an acid condition, but that of itself it is not likely to produce harmful effects unless present in very large amts. The toxicity of certain soil exts. was apparently due more to the acidity of the soln., or to the combined effect of acid and Al, than to the Mn, which was frequently found. The results obtained by means of seedling cultures in soil exts. indicated that  $MgCO_3$  may lower the acidity of such exts. and thus render the solns. better mediums for growth. Efforts to det. whether salts of Al were toxic, more because of the acidity of such salts than because of the direct effect of the Al, gave disappointing results, since the Al could not be kept in soln. when the acidity was destroyed. Certain plants, like velvet beans and peanuts, appeared to be more able to throw the Al out of soln. by neutralizing the acid than other plants, such as clover or *Melilotus* seedlings. In recent work several soils from north Alabama gave very acid exts. after incubation with dried blood. It was shown that each of these soils from which very acid exts. were obtained supported nitrification of dried blood, and that sol. Mn was present in large quantities in most cases. This work is to be continued. H. G.

**The chemical composition of Bordeaux mixture.** A. WÖBER. *Z. Pflanzenkrankh.* 29, No. 3-4, 94-104(1919); *Expt. Sta. Record* 43, 444.—This deals with what is known or thought regarding the acid, the neutral, and the alk. phase of Bordeaux mixt. The last named is regarded as the most durable and reliable as a fungicide for use on foliage. H. G.

**Preliminary report on chemical weed control in coniferous nurseries.** P. C. KIRCHIN. *J. Forestry* 18, 157-9(1920); *Expt. Sta. Record* 43, 42.—A brief summary of results thus far secured in several National Forest nurseries, including tabular data on work done by E. C. Rogers at the Savenac nursery, Haugan, Mont. Although the work at Savenac was done primarily with the view of controlling damping-off fungi



through the use of chemicals, records were also kept of weed growth on the various plots during 1917. The results obtained indicate that Zn and Cu salts may be efficient in destroying weeds shortly after germination, at least in the type of soil used. Expts. have been continued at Savenac with different strength solns. of  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ , and  $\text{ZnCl}_2$ . H. G.

**Field experiments on the chemotropic responses of insects.** A. D. IMMS AND M. A. HUSAIN. *Ann. appl. biol.* 6, 269-92(1920); *Expt. Sta. Record* 43, 553-4.—The most noteworthy features of the expts. here reported have been summarized as follows: The experiments were conducted during July and August, 1918, and for the most part during wet and apparently unfavorable climatic conditions. The insects attracted consisted almost exclusively of Diptera. With the exception of one or two examples of *Vespa vulgaris*, no Hymenoptera responded. Rynchocha, Coleoptera, and Neuroptera (sen. lat.) were unrepresented. A small number of Noctuid Lepidoptera entered the traps, but for the purpose of conducting expts. with such relatively large insects as many Lepidoptera it would be necessary to alter slightly the construction of the traps used in order to allow of greater facilities for ingress. Beer, cane molasses, and mixts. of these two substances are powerful chemotropic agents for various Diptera. EtOH, in various concns., exhibited little or no chemotropic properties, but with the addition of small amts. of butyric, valeric, or acetic acids it exercised a powerful stimulus. Aq. solns. of the above acids were not attractive, the respective esters probably being the attractive agents in each case. The remaining substances utilized in these expts. were found to exhibit little or no positive chemotropic properties. H. G.

**Report of committee on agricultural progress of the Louisiana Sugar Planters Assoc. (GOUAUX, et al.)** 28. A dry method of preparing lead arsenate (BROWN, et al.) 18. The biochemistry of tobacco. II. Tobacco seeds (PARIS) 11D. Peat in 1919 (COTTELL) 21. The Przibilla tartrate method for potassium (BORSCHÉ) 7.

**FELTZEN, H. VON:** What Significance has Peat Litter for a Better Conservation of Natural Fertilizers, especially in view of the Prevailing High Prices of Artificial Fertilizers? Örebro, (Sweden): Örebro New Printing Co. 20 pp. For review see *Expt. Sta. Record* 43, 423(1920).

## 16—THE FERMENTATION INDUSTRIES

H. S. PAINE

**Alcohol and the chemical industries.** J. M. DORAN. Internal Revenue, Washington. *J. Ind. Eng. Chem.* 13, 564-5(1921).—An address, historical and critical, dealing with the denaturing problem. Hope is expressed for the manu. of a universal denaturant which shall be non-poisonous, leave the alc. useful in therapy, yet unfit to drink, and above all be inactive for use in chem. industries. C. C. DAVIS

**Industrial alcohol and its relation to prohibition enforcement from the manufacturers' standpoint.** M. C. WHITAKER. *J. Ind. Eng. Chem.* 13, 647-50(1921). E. H.

**Present outlook for industrial alcohol.** H. I. PEPPER. *Sugar* 23, 213-5, 254-5(1921).—The production of industrial alc. in 1918 was 178,833,799 gallons. Production in the U. S. is principally from blackstrap molasses. The cheapness of this product and the ease with which it is utilized makes it the most economical product. Numerous by-products of fermentation are now used for commercial purposes. A number of uses of alc. which have been developed recently are described. C. H. CHRISTMAN

**Production of industrial alcohol on sugar estates.** E. W. DEMING. *Louisiana Planter* 66, 221(1921).—Five gal. molasses, yielding 0.4 gal. alc. per gal. of molasses,



is available for every ton of cane ground. A sugar house grinding 2000 tons daily could operate a distillery of 2000 gal. capacity the entire year. The alc. value of molasses is 12.5 cents per gal. The fertilizer value of the unfermented residue is about 4 cents per gallon of molasses.

C. H. CHRISTMAN

**The manufacture of potash salts as by-products in sugar-cane distilleries.** MAURICE BIRO. *Louisiana Planter* 66, 237 (1921).—The refuse liquor from fermented molasses, after distn. of the alc., is evapd. in troughs by means of flue gases. The residue is charred and KCl and  $K_2SO_4$  are extd. A moderate sugar crop removes 80 lb. potash per acre.

C. H. CHRISTMAN

**Value of Halphen's rule for Italian wines.** F. SCURTI AND E. ROLANDO. *Giorn. chim. ind. applicata* 2, 330 (1920).—As a result of their expts., the authors drew the following conclusions: Halphen's rule for the detn. of watering of wines, applied according to criteria set down by Posetto and Issoglio, to wines from many Italian regions, gave uncertain and fallacious results. Genuine wines with a ratio less than calcd. by an amt. exceeding  $-0.120$ , were found in the most important wine centers. Wines high in acidity can tolerate addition of  $H_2O$  up to 25% and still give a good value for the ratio acidity : alc., and still be apparently genuine.

ROBERT S. POSMONTIER

**Fluorine in Italian wines.** C. E. ZAY. *Giorn. chim. ind. applicata* 2, 397 (1920).—Z., analyzing a large number of wines for F by the Treadwell method, found only un-analyzable traces. To decide if wines could take up F from soils containing it in large amts., Z. cultivated vines for 2 yrs., watering them daily with 200 cc. of alk. fluoride solns. of from 1% to 0.25% and less. In the wines obtained from the grapes of these plants, no F, except in extremely small amts., was found. Hence Z. concluded that com. wines containing F in appreciable amts. must be looked upon as having been sophisticated with this element.

ROBERT S. POSMONTIER

**Behavior of artificial coloring materials added to wine.** F. SCURTI AND E. RUATA. *Giorn. chim. ind. applicata* 2, 329 (1920).—This investigation was undertaken to find out how much account must be taken of the observed facts that artificial coloring substances in wine tend to disappear in certain cases with lapse of time. The authors drew the following conclusions from their work: (1) The disappearance of coloring materials in wines depends principally upon the content of the wine itself in protein substances and in pathogenic organisms. (2) Tannin substances exert also an appreciable action, since artificial coloring substances tend to disappear from red wines sooner than from white wines. (3) Artificial coloring substances tend to disappear more rapidly in musts than in wines, more rapidly in incompletely fermented wines than in dry wines, in altered than in whole wines. (4) Organized agents differ from org. agents in their greater field of action. While protein substances and tannins or tanning materials are capable of driving out coloring substances of acid nature only, disease germs may deprive a wine of added artificial colors, whatever be the nature of these substances. (5) Hence it is evident that if an artificially colored wine subjected to analysis becomes altered as a consequence of disease, the absence of coloring substance verified later does not furnish indication for invalidating the analysis previously made. (6) If the wine remains whole and a second loss of substance is discovered, 2 cases may be distinguished: (a) If the artificial coloring substance was of acid nature: in this case the second analysis, especially if made much later, has very little value, because the artificial coloring substance might have combined with albuminoid and tannin substances of the wine, and become unrecognizable analytically. (b) If the artificial coloring substance was of basic nature: in this case the finding of loss of coloring substance is of full value, because basic coloring substances remain practically unaltered in whole wines.

R. S. P.

**Cyanided wine and the iron casse.** Ph. MALVÉZIN. *Ann. chim. anal. chim. app.* 3, 154-5 (1921).—M. in examg an Algerian wine found free HCN by the picric acid test



and believed it due to the use of an excessive amount of ferro- and ferricyanides in the removal of the casse due to iron. HCN may come from the reaction of the excess cyanide with the  $H_2SO_4$  owing to sulfuring or with the tartaric acid of the wine. Also in *Ann. fals.* 14, 152-3(1921).

H. A. LEPPER

**The determination of iron in wine.** L. MATHIEU. *Ann. chim. anal. chim. appl.* 3, 106(1921).—Malvezin and Rivalland (*C. A.* 15, 1674) have been unable to obtain satisfactory results with Mathieu's KCNS test but this is perhaps due to unfavorable visual conditions. M. has, in fact, obtained better results than he claimed. Recently the method (*C. A.* 14, 3033) has been modified slightly by using 10%  $H_2SO_4$  to dissolve the Fe in the ash rather than 25% HCl so that the liquid can be boiled without fear of losing acid. Also in *Ann. fals.* 14, 203-4(1921).

W. T. H.

**Cider-making experiments for the season 1918-19.** OTTO GROVE. Univ. Bristol. *Ann. Rept. Agr. and Hort. Research Sta.* 1919, 14-7.—Four mixed varieties, 2 single variety ciders and one perry were prepd. in a study to test means to increase the output of cider in seasons of scarcity based on soaking the pomace, adding the 2nd pressing to the 1st and fortifying with sugar. Fermentation was normal but slower and products while palatable were not of as good quality as av. pure fruit juices. H. A. LEPPER

**Some experiments on ropiness in cider.** OTTO GROVE. Univ. Bristol. *Ann. Rept. Agr. and Hort. Research Sta.* 1919, 18-9.—Eight ciders were inoculated with 2 drops of pure culture of bacillus previously found as the cause of ropiness in cider (*C. A.* 14, 2039). Neither expt. nor control samples developed rope in one year but all except one expt. and 2 controls developed it at end of this period. H. A. LEPPER

**The relation between the rate of fermentation and the content of nitrogenous matter in apple juice.** OTTO GROVE. Univ. Bristol. *Ann. Rept. Agr. and Hort. Research Sta.* 1919, 20-2.—The juices of six varieties of apples were sterilized in Erlenmeyer flasks, inoculated with pure yeast, and closed with  $H_2SO_4$  trap. The rate of fermentation was followed by weighing and when finished, verified by cessation of yeast growth detd. microscopically, sugars, N, and sp. gr. were detd. Rapid complete fermentation of four juices left only traces of sugar and 0.0135-0.0221% N while the other two showed 6.3 and 1.04% sugar and 0.0033 and 0.0094% N. If some nitrogenous yeast food ( $(NH_4)_2SO_4$ , yeast ext.) is added to juices deficient in N, fermentation will proceed rapidly until dry. No satisfactory method to check fermentation by depriving the juice of N without otherwise changing its chem. compn. is available. H. A. LEPPER

**The influence of vinegar eels on the composition of vinegar.** N. PASSERINI. *Bol. Soc. Ital. Studio Aliment.* 2, No. 1-2, 1-5(1920); *Expt. Sta. Record* 44, 117.—Samples of vinegar of low initial acidity (2.8% calcd. as AcOH) were treated as follows: One sample was sterilized, three were sterilized and then inoculated with vinegar eels, two were simply filtered, and one was inoculated with the eels. All samples were stored under like conditions for 11 months and then analyzed for acidity, dry ext., and ash. The original acidity was maintained in the sterilized samples, was decidedly decreased in the filtered samples contg. no vinegar eels, and was increased in all samples contg. the eels. Observations during the period of storage had shown that in the tubes contg. vinegar eels a light film of the mother of vinegar persisted on the surface of the vinegar, while in those contg. no eels the film grew rapidly and finally settled to the bottom of the tube. In explanation of these observations, P. concludes that the vinegar eels prevent too rapid growth and settling of the mother of vinegar and thus assist in the normal surface oxidation of the vinegar, while the submerged mother of vinegar brings about the decompn. of the AcOH into  $CO_2$  and water.

H. G.

**Natalite and the world's motor fuel position (ANON) 21.** Sugar and alcohol from the agave (DELAFOOND) 28.



## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**Cello-Kresol.** J. E. BRAUER-TUCHORZE. *Chem. Ztg.* 45, 97(1921).—A new disinfectant, Cello-Kresol, is highly recommended for a wide variety of uses. It contains approx. 20% of cresols and a high % of hydrocarbons of high mol. wt. With H<sub>2</sub>O it forms a milk-white permanent emulsion in all proportions. A 1% soln. will kill many of the common bacteria, such as the staphylococci, within 10 min., and solns. of similar concns. will disinfect stables, stalls, aviaries, henneries, and the like. A 0.5-1% soln. is an effective spray for fruit and garden culture. C. C. DAVIS

**Chemico-toxicological test for morphine.** DOMENICO GANASSINI. *Boll. chim. farm.* 60, 2-5(1921).—The Denigès color reaction can be applied as a test for morphine in blood by using the following technic. Dil. 1 cc. blood with 40 cc. distd. H<sub>2</sub>O and add 10 drops concd. HNO<sub>3</sub>. Filter off the brown ppt. of globulin and hematin. Treat the colorless filtrate with 1 cc. ammoniacal CuSO<sub>4</sub> (prepd. from 20 cc. concd. NH<sub>4</sub>OH and 5 cc. 0.5% CuSO<sub>4</sub> soln.) and 10 drops H<sub>2</sub>O<sub>2</sub> (perhydrol dild. with equal vol. H<sub>2</sub>O). If traces of morphine are present the liquid rapidly assumes a more or less intense rose color. The same procedure can be used in testing milk or urine, omitting the HNO<sub>3</sub>, but the reaction is less delicate. Oxymorphone and the alkaloids which accompany morphine do not give this reaction. Synthetic derivs. of morphine, such as diionine and perionine, do not give the test, while heroine, contrary to the statement of Denigès, responds readily. It is probable that heroine (diacetylmorphine) contains a free phenolic OH, one acetyl being attached to the alcoholic OH and the other to the phenanthrene ring or to the side chain. Heroine is readily distinguished from morphine by the Goldman, Zernick, and Mauseau reactions. A. W. DOX

**Popular therapeutic empiricism in Rome.** ANON. *Boll. chim. farm.* 60, 5(1921).—A list of popular remedies used in Rome up to the past century for the treatment of various ailments. A. W. DOX

**Rhizome of *Phragmites communis* Trin., especially its sugar content.** TH. SABALITSCHKA. *Arch. Pharm.* 259, 102-10(1921).—The investigation was undertaken in refutation of certain extravagant claims made for this product by exploiting agencies during and since the war. Analysis of the powdered rhizome shows the following compn. H<sub>2</sub>O 5.3%, nitrogenous substances 5.2% (6.25 factor), fat 0.9%, N-free extractives 50.8%, crude fiber 32%, ash 5.8%. The quantity of sucrose based on inversion data was found to be 5.08%. W. O. E.

**Pelargonium oil.** RICHARD KNUTH. *Am. J. Pharm.* 93, 376-87(1921); cf. C. A. 15, 2334.—Chem. constitution of the oil with bibliography appended. W. G. GAESSLER

**Studies in extraction.** JAMES F. COUCH. *Am. J. Pharm.* 93, 419-26(1921).—Results of an inquiry into the factors which govern the rate of extn. of *Phytolacca*, the generalizations which underlie it, and the conditions which obtain are summarized as follows: The extn. of the root of *Phytolacca* proceeds regularly with diminishing velocity. The rate of extn. is proportional to the total ext., inversely proportional to the residual extractive, the time, and an unknown factor or combination of factors. On account of these unknown factors a number characteristic of the extractibility of the drug cannot be assigned it. It is probable that the unknown factors depend upon a change in the compn. of the ext. and a rise in the alc. content of the percolate. The first fifteen gallons of percolate contained 97% of the total matter extd. It is shown that the alc. content of the percolate increases as the percolation proceeds. This has not hitherto been demonstrated. W. G. GAESSLER

**The assay of aconite.** A. R. DOHME. *Am. J. Pharm.* 93, 428-9(1921).—D



reports results obtained during the past three years by the Scientific Section of the American Drug Manufacturers' Association, which recommends that the chemical assay be dropped for aconite and its preps. and a physiological assay based upon aconitine crystallized U. S. P. be substituted in its place.

W. G. GAESSLER

**Podophyllum ash standards.** E. L. NEWCOMB, C. H. ROGERS, AND C. W. FOLKSTAD. *Am. J. Pharm.* 93, 429-32(1921).—There is considerable variation in the proportionate amount of roots and rhizomes; these parts are sometimes plump and sometimes shriveled. Plump starchy roots and rhizomes contain a proportionately small amt. of  $\text{CaC}_2\text{O}_4$  and yield a low ash. Shriveled roots and rhizomes contain less starch, proportionately more  $\text{CaC}_2\text{O}_4$  and yield a high normal ash. Some commercial lots of the drug consist almost entirely of plump or bold roots and rhizomes. Others represent a mixt., while still other lots consist chiefly of shriveled roots and rhizomes. An excess of inorganic foreign matter has no doubt been responsible for much of the difficulty with the ash standard.

W. G. GAESSLER

**Studies on licorice root and licorice extract.** PERCY A. HOUSEMAN. *Am. J. Pharm.* 93, 481-85(1921).—The method of Linz for the detn. of glycyrrhizin in licorice ext. is discussed. A method is given for the detn. of glycyrrhizin in licorice ext. Comparative expts. have been made on various methods for sepg. part or all of the resins and bitter principles from licorice root, before proceeding to the detn. of glycyrrhizin. A method is given for the detn. of glycyrrhizin in licorice root, involving removal of resins with ether, followed by extn. of glycyrrhizin with 75% alc. The figures for glycyrrhizin in licorice root, published by other investigators and in books, are too low. The other constituents of licorice ext. and root, which may be advantageously included in an analysis, are mentioned.

W. G. GAESSLER

**Some notes on the astringencies of red rose and pale rose.** JOSIAH C. AND BERTHA L. DEG. PEACOCK. *Am. J. Pharm.* 93, 497-500(1921).—"The tannin of red rose" is present in pale rose as well, but in a very much less proportion, perhaps less than 1% of its wt. Except for the much smaller proportion of astringency and the relatively greater bitterness, the physical properties of the infusions of the two roses were found to be very similar, while behavior toward reagents further demonstrated a similarity of ingredients. Isolation of a cryst. principle which seemed to develop under the influence of mildew growth upon an unstrained infusion of red rose is reported. The expts. will be repeated to det. whether the crystals will develop in the mush (a mixt. of ether-exhausted red rose and water) without the appearance of mildew.

W. G. GAESSLER

**Sour salt, a new synonym for tartaric acid or citric acid.** CHARLES H. LA WALL. *Am. J. Pharm.* 93, 496(1921).—Upon investigation it was found that the product sold by some firms, instead of consisting of tartaric acid or citric acid, was composed wholly or in great part, of alum crystals.

W. G. GAESSLER

**Experiments with iodine-neol preparations.** DORNIS. *Z. Veterinar.* 32, No. 2, 27-8(1920); *Expt. Sta. Record* 43, 683-4.—A substitute for I as a disinfectant is described consisting of a soln. of one part of free I and three parts of a compd. of I with ricinoleic acid. This mixt. is insol. in water, difficultly sol. in alc., and readily sol. in ether-alc., ether,  $\text{CHCl}_3$ ,  $\text{CS}_2$ , and essential and fatty oils. The I-neol is dispensed either as a powder, in a sterilized bolus with tale, as a tincture in ether-alc., or incorporated in a soap salve. D. has demonstrated the value of the I-neol bolus in wounds for which an open dressing is indicated. As an antiseptic under permanent dressings, as in the case of hoof operations, the tincture is preferred. The latter in concd. form is recommended as a mild caustic, and, diluted with one or two parts of alc., as a disinfectant for infected wounds of all kinds. It is also recommended for skin disinfection before operations and in the treatment of skin diseases of parasitic and nonparasitic nature.

H. G.



Essential oils and their substitutes. P. MAVER. *Z. wiss. Mikros.* 36, 219-56 (1920); *Physiol. Abstracts* 6, 5.—A description is given of the properties of 19 ethereal oils and of their applications in microscopic technic, together with an account of substances which can be used as substitutes. The most difficult to replace is cedar-wood oil.

H. G.

A chemical study of *Lythrium salicaria*. J. R. CARRACIDO AND A. MADINAVEITA. *Anales soc. españ. fis. quim.* 19, 148-51 (1921).—This plant is used in many countries as an unofficial remedy for diarrhea. It grows in damp saline places. Its ash contains twice as much sodium as potassium. The plant contains a reducing sugar, a glucoside, tannin, an unusual amt. of iron, and 0.028% of choline.

L. E. GILSON

The possibility of an essential oil and natural perfume industry in the Argentine Republic. JOSÉ ALAXRAQUI. *Anales soc. quim. Argentina* 7, 440-50 (1919).—Actual expts. over a number of years have shown that all of the plants cultivated in Europe for the sake of their volatile oils will grow readily in some parts of Argentina and will give a yield of oil equal in quantity and quality to the European products.

L. E. GILSON

The necessity for accurate statement of the conditions for extracting senna by alcohol. E. MAURIN. *Bull. sci. pharmacol.* 28, 295-99 (1921).—The results of these briefly reported expts. indicate that senna should be extd. with 95% alc. by maceration for 48 hrs. in the ratio of 1:4.

F. S. HAMMETT

Tests for oil of cade. R. HUERRE. *Bull. sci. pharmacol.* 28, 299-303 (1921).—H. demonstrates that certain so-called oils of cade fail to give either the Cu acetate test or the adequate return by fractional distn. between 150 and 300°, both of which tests are given by the genuine material obtained from incomplete combustion of the wood of *Juniperus oxycedrus*.

F. S. HAMMETT

The methods for testing cardiac drugs. ARNOLD HOLSTE. *Z. exp. Path. Therap.* 22, 1-21 (1921).—From a comparison of the action of drugs on the frog when injected into the lymph sac, the venous system, or to the isolated heart, it is concluded that the last method is most reliable.

F. S. HAMMETT

Progress in the field of ethereal oils and the chemistry of the terpenes in 1920. K. BOURNOT. *Chem.-Zig.* 45, 560-71, 586-7, 590-1 (1921).

E. H.

The chemistry of neoarsphenamine and its relation to toxicity. GEORGE W. RAIZISS AND M. FALKOV. Dermatological Research Lab., Phila. *J. Biol. Chem.* 46, 209-21 (1921).—Com. samples of neoarsphenamine from 3 different labs. were analyzed. A low As content is due to the presence of impurities such as uncombined Na formaldehydesulfoxylate,  $\text{Na}_2\text{SO}_4$  and NaCl. Loss on drying to const. wt. indicates  $\text{MeOH}$  or  $\text{H}_2\text{O}$  of crystn. The As : N ratio can be regarded as a comparatively good indicator of the purity of the compd. The amt. of combined sulfoxylate found is greater than that necessary for one amino group and less than the calcd. value for both amino groups, indicating that neoarsphenamine is a mixt. of both the mono- and disubstitution products; the formula for the latter is  $(\text{NaO}_2\text{SCH}_2\text{N}(\text{HO})(\text{C}_6\text{H}_5)\text{As})_2$ . Variation in the completeness of substitution in the amino groups probably accounts for the irregularity of the toxicity and therapeutic effect of the drug.

A. P. LOTHROP

Action of aspirin on urethan. E. COMANUCCI. *Rend. accad. sci. Napoli* 27, 47-52 (1921).—Mixts. of aspirin and urethan at ordinary temps. present neither chem. nor physical incompatibilities, but when heated to fusion reaction takes place at about 90-5°, giving salicylic urethan and  $\text{AcOEt}$  if the temp. does not rise above 130°, while at 180-2°  $\text{CO}_2$  and  $\text{NH}_3$  are evolved, and at about 200° PhOH is formed, with a yellow substance, slightly sol. in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  and  $\text{CHCl}_3$ , and containing salicylamide and salicylonitrile. Another compd. containing N is formed, m. 227°, sol. in  $\text{H}_2\text{O}$  and  $\text{EtOH}$ , insol. in  $\text{Na}_2\text{CO}_3$ , easily sol. in  $\text{NaOH}$ , and probably consisting



of carbonylsalicylamide,  $C_6H_4OCO.NH$ , formed by loss of  $H_2O$  from salicylic urethan.

M. R. SCHMIDT

**Properties and analysis of benzyl benzoate.** J. J. HOFMAN. *Pharm. Weekblad* 58, 430-4(1921).—The properties by which  $BzOCH_2Ph$  is most readily characterized are: sapon. no., sp. gr., m. p. (about  $20^\circ$  after congealing in a freezing mixt.) and b. p. The b. p. at 1 atm. is above  $360^\circ$ , though given in the literature as  $323-4^\circ$ . The ester is volatile with steam. Odor and taste may sometimes aid in identification. It is completely miscible with nearly all org. solvents and with peanut, olive and many other vegetable oils, and miscible with 2-3 vols. of liquid paraffin or castor oil. It is insol. in  $H_2O$  and in glycerol, sol. in 3 pts. of MeOH. It gives clear solus. with aq. EtOH as follows: 1:1 at  $26^\circ$ , 1:1.5 at  $21^\circ$ , 1:2 at  $18^\circ$ , 1:2.5 at  $16^\circ$ . In dil. alc. (41 wt. % of EtOH) it gives clear solus. in the proportions: 1:10 at  $59^\circ$ , 1:20 at  $31^\circ$ , 1:28 at  $20^\circ$ , 1:33 at  $15^\circ$ . It is not easily hydrolyzed nor oxidized. Conc'd.  $H_2SO_4$  (80% or stronger) resinifies it. For patients to whom no alc. should be given it is best emulsified with licorice ext. Its trade names are "spasmodin," "peruscabin," "peruol" (a 25% soln. in castor oil) and "peruol cream" (a 25% paste in potash soap cream).

JULIAN F. SMITH

**Mezereon ointment.** W. F. WOUTMAN. Amsterdam. *Pharm. Weekblad* 58, 496(1921).—A description of the prepn. of ointment from mezereon (garoo) bark. The consumption of alc. amounts to about 5 kg. per kg. of ointment produced.

JULIAN F. SMITH

**Cubeb extract.** W. F. WOUTMAN. Amsterdam. *Pharm. Weekblad* 58, 496-7(1921).—Old cubebs sometimes yield as low as 16% of ext., instead of the usual 19.2-21.7%. This is probably due to partial resinification of the essential oil. The pharmacopoeia should specify a max. age for cubebs to be used for making ext.

JULIAN F. SMITH

**Opium extract.** W. F. WOUTMAN. Amsterdam. *Pharm. Weekblad* 58, 497-8(1921).—In prepg. opium ext., a considerable fraction of the water sometimes remains in the press cake. This can be detected by weighing before the extn. and weighing the press cake. If the amt. retained is considerable another maceration with water is advisable.

JULIAN F. SMITH

**Liquor carbonis detergens.** W. F. WOUTMAN. Amsterdam. *Pharm. Weekblad* 58, 498(1921).—Liquor carbonis detergens, made from coal tar and tincture of soap bark, can be more cheaply made with crude than with purified coal tar. The yield is somewhat less, but the saving on the tar more than compensates.

JULIAN F. SMITH

**Purified oil of turpentine.** W. F. WOUTMAN. Amsterdam. *Pharm. Weekblad* 58, 498-9(1921).—In refining turpentine by distg. with 6 parts of water in presence of  $Ca(OH)_2$ , it is permissible to distil off 90% instead of 75% of the liquid. The product still conforms to the requirements of the Pharmacopoeia. The last 15%, if collected separately, shows a slight yellow color and leaves a trace of residue when evapd. If rejected for this reason, it is still quite satisfactory for use in the further prepn. of refined turpentine, or for any purpose for which crude turpentine is used.

JULIAN F. SMITH

**Active constituents of shepherd's purse.** H. W. VAN URK. *Pharm. Weekblad* 58, 553-6(1921).—According to Hager (*Pharmazeutisches Praxis* I, 604), *Capsella bursa pastoris* contains an unstable alkaloid, a glucosidic acid (bursaic acid?) and allyl mustard oil. Blanksma (*C. A.* 9, 1613) showed that the last-named substance was in reality a compd. of the mercaptan type. Tests for alkaloids and glucosides were negative, tending to indicate that bursaic acid is not glucosidic and that all 3 of H.'s statements are erroneous. Other investigators are invited to carry the study farther.

JULIAN F. SMITH

**Mistletoe, a plant which contains urson.** E. I. VAN ITALLIE. Amsterdam. *Pharm.*



*Weekblad* 58, 824-5(1921).—Urson was obtained from 2 varieties of *Viscum album* (1 from apple trees, 1 from poplars) by extg. with alc., allowing the ext. to stand several weeks, taking up the ppt. in Et<sub>2</sub>O, evapg. and recrystallizing several times from EtOH. The substance gave all the urson tests described by Nooyen (Dissertation, Leyden 1920) except that the m. p. was about 287° instead of 272-4°. The plant from apple trees yielded more urson than that from poplars. This is probably connected with the fact that the former variety bears berries while the latter does not. The berries may be expected to have a relatively high urson content. This point is to be studied during the bearing season.

JULIAN F. SMITH

**Solubility of drugs in glycerol.** HOLM. *Pharm. Weekblad* 58, 860-2(1921).—Existing data on soly. of drugs in glycerol are meager and conflicting, and never state the strength of glycerol used. Detns. at 20°, made both by dissolving the samples in the cold and by dissolving at 90°C. and cooling to 20° till equil. was reached, gave results which differ widely from those stated in the literature. Figures are given, in g. of substance sol. in 100 g. of solvent, for 86.5% and 98.5% glycerol, resp.: Pb(OAc)<sub>2</sub>, 129.3, 143.0; BzOH 1.18, 2.0; H<sub>3</sub>BO<sub>3</sub> 13.79, 24.80; salicylic acid 0.985, 1.63; Na borate 89.36, 111.15; KBr 20.59, 17.15; KClO<sub>3</sub> 1.32, 1.03; KI 58.27, 50.70; quinine sulfate 0.72, 1.32. Some substances, when heated to 90° with glycerol and cooled to 20°, take months to crystallize. For some the soly. cannot be detd. because of compd. formation. Thus, it was found that 58% of dissolved tartaric acid may be present as the neutral ester.

JULIAN F. SMITH

**Protection of drugs against the action of light.** J. B. M. COEBERGH. *Pharm. Weekblad* 58, 865-6(1921); cf. *C. A.* 15, 922.

JULIAN F. SMITH

**Chenopodium oil.** P. VAN OER WIELEN. *Pharm. Weekblad* 58, 866-8(1921).—A review of the culture, use and methods of examn. of chenopodium oil. J. F. S.

**A reaction to differentiate natural and synthetic camphor.** UTZ. *Farben-Ztg.* 26, 1065(1921).—Investigations by U. show that the methods of Lenz (*C. A.* 5, 2528) and of Zimmerman (*Apoth. Ztg.* 35, 382(1920)) do not differentiate between natural and synthetic camphor, and that his vanillin-HCl reaction (*C. A.* 2, 887) is still the best for detecting natural camphor although it will not detect synthetic camphor. (See *C. A.* 1, 2622; 2, 539; 9, 1664.)

F. A. WERTZ

**Iodine compounds of sugars.** SHIKIJI MIYASHI. Japan 36,702, July 5, 1920. Milk, grape, fruit, or invert sugar or honey is mixed with excess of Ca(OH)<sub>2</sub>, boiled, and filtered. The filtrate is satd. with CO<sub>2</sub>, boiled and filtered. The filtrate is evaporated to dryness and dissolved in a small quantity of warm H<sub>2</sub>O, to which 12.359% I is gradually added. After the reaction is completed, the soln. is evapd. to dryness, yielding yellowish brown powder, easily sol. in hot H<sub>2</sub>O and stable toward sunlight or acid. It has therapeutic properties.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

F. C. ZEISBERG

**Sulfuric acid.** S. PAGLIANI. *Ann. chim. sci. ind.* 37, 53-79(1921).—Review of the manuf. of H<sub>2</sub>SO<sub>4</sub>, including the contact process and the concn. of dil. acid. Cf. *C. A.* 14, 2529.

R. FIERTZ

**Sulfur recovery from blast-furnace slag.** L. B. DIRMIL. *Stahl u. Eisen* 41, 815 (1921).—Since Germany is dependent upon imported raw materials for H<sub>2</sub>SO<sub>4</sub> manuf. it is very desirable to find a source of S within the country. Before the war 20 million tons of blast-furnace slag were produced annually contg. an av. of 1.5% S. This con-



responds to at least 300,000 t. of S which is lost. The Diehl process consists in blowing air or O through the liquid slag with or without the addition of gypsum. The CaS of the slag is thereby oxidized to CaO, which dissolves in the slag and SO<sub>2</sub>, which is evolved. This process gives a gas containing about 23% SO<sub>2</sub> if O is used or 6-9% if air is used. Details of the practical application of the method are given. R. S. DEAN

**The manufacture of citric acid from lemons.** C. P. WILSON. Corona, Cal. *J. Ind. Eng. Chem.* 13, 554-8(1921).—A detailed description, historical and technical, of the present process in California for extg. citric acid from low-grade lemons. One ton of lemons contains an av. of 70 lbs. of acid (caled. as crystd. citric acid), of which about 85% is extd. in the juice. C. C. DAVIS

**A dry method of preparing lead arsenate.** O. W. BROWN, C. R. VORIS AND C. O. HENKE. Indiana Univ. *J. Ind. Eng. Chem.* 13, 531-3(1921).—An investigation of the reaction between PbO and As<sub>2</sub>O<sub>3</sub> by roasting in a rotatory furnace. It was found that (1) Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> is produced by roasting PbO and As<sub>2</sub>O<sub>3</sub> at high temp., (2) roasting at 450° gives the best results in yield and economy, (3) oxidation is at first very rapid, with subsequent slow rate, and (4) catalytic action is probable. Some As is volatilized before it combines with PbO and the lower the temp. the longer the duration of the loss, but the slower the rate. Roasting at any temp. over 300° results in a very slow rate of oxidation after the first hr. Plots show the relation between the rates of oxidation and the temp. At 450° the oxidation rate is most rapid with an ultimate max. yield. This temp. also gives the max. yield of Pb<sub>3</sub>O<sub>4</sub> from PbO, showing that PbO perhaps acts as catalyzer in oxidizing to Pb<sub>3</sub>O<sub>4</sub>, which in turn oxidizes As<sub>2</sub>O<sub>3</sub> to As<sub>2</sub>O<sub>5</sub>. If an auxiliary catalyst is used, to be most effective it should oxidize most easily at the temp. at which the desired oxidation is most easily effected. Methods of analysis are given. C. C. DAVIS

**Manufacture of potassium bitartrate and tartaric acid.** H. VOSS. *Chem. Ztg.* 45, 309-13, 335-7, 360-4, 411-2(1921).—Bitartrate is produced from crude tartar containing at least 60% bitartrate by repeated crystn. with intervening decolorizations. The lees are crushed in a ball mill to pass 50-mesh dissolved in H<sub>2</sub>O, and the insol. material is removed by decantation or filter-pressing. For production of 500 kg. KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, 11,500 kg. mother liquor at 90° are needed, of this about 500 kg. are lost by evapn., spilling, and absorption before crystn. The first product is about 527 kg., "brown crystals;" these are washed with cold H<sub>2</sub>O with loss of 1%, leaving 522 kg. containing 15.66 kg. alkaline earths calcd. as CaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>. To remove these, 6.25 kg. HCl are required. This is added to the brown crystals barely covered with cold H<sub>2</sub>O, the mixt. stirred a few times and allowed to settle; the liquor containing the chlorides is drained through a Cu screen, and the crystals are washed 3 times with cold H<sub>2</sub>O (about 250 l. to each 100 kg. crystals); about 19.5 kg. of bitartrate are lost in this process. The brown crystals are next dissolved in "white liquor," 1-2% animal charcoal (HCl extd.) is added, the soln. boiled 30 min., allowed to stand 2-3 hrs., the liquor drawn off, allowed to crystallize 3 days and the white liquor removed. Crystals are drained and dried at 50-60°. Two general processes with modifications of each are described for tartaric acid. The alkali or neutral process converts bitartrate to CaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> by CaO, CaSO<sub>4</sub>, or CaCl<sub>2</sub> and the product to tartaric acid by H<sub>2</sub>SO<sub>4</sub>. In the acid or sour process the bitartrate is treated with HCl or H<sub>2</sub>SO<sub>4</sub>. Soln. is effected cold or hot and at normal or higher pressures. Pptd. and suspended materials are removed and evapn. is followed by crystn. The acid process requires twice as much mineral acid as the neutral but the final liquors are purer in the former. All calcns., chem. and mechanical, required in the operations are carried through and each step is described in detail. The raw material should be sterilized in boilers or, preferably, roasters. This not only prevents fermentation but makes subsequent operations less difficult. About 25% of tartaric acid remains within the



process, passing through a cycle. Calcs. involved are shown by 70 equations, and 13 detailed work tables show quantities of reagents of all needed dilns. required. G. R. J.

**The nitrate industry of Chile.** U. S. Dept. Com., Bur. Foreign and Dom. Com., Com. Repts. 1920, No. 122, 1093-1103; *Expt. Sta. Record* 43, 728.—This is a report on the general features of the mining and refining of Chilean nitrate. It is stated that two grades of nitrates are now produced, namely, a 95% nitrate, which is used for fertilizer purposes, and a 96% nitrate, used for mfg. purposes. Imports of  $\text{NaNO}_3$  into the United States for the year 1919 were 407,459 long tons. Apparently a relatively small proportion of the nitrate imported into the United States from Chile is used for fertilizer purposes. H. G.

**French potash.** H. VON FEILITZEN AND I. LUGNER. *Svenska Mosskulturfor. Tid.* 34, No. 5-6, 351-56(1920); *Expt. Sta. Record* 44, 515.—Comparative analyses of samples of Alsatian and German 20 and 50% potash salts showed that the Alsatian 20% salt contained only slightly more KCl than the German salt, considerably more NaCl, and not nearly as much sol. magnesia. The 50% German salt contained more KCl than the Alsatian salt and less NaCl. Mixts. of superphosphate with the German and Alsatian 20% salts showed practically no reversion of the superphosphate after storage for one week. H. G.

**The potash of Alsace and potash of Germany.** A. ARNAL. *Vie agr. rurale* [10] 1920, No. 6, 98-100; *Expt. Sta. Record* 42, 723.—A comparison is given of the value of the potash resources of Alsace and of Germany. It is the opinion that the German potash is inferior in grade and purity to that of Alsatian potash, and that the process of extn. is more difficult. Other factors of advantage of the Alsatian potash are discussed. H. G.

**Sources of industrial potash in Western Australia.** E. S. SIMPSON. *West Aust. Geol. Survey Bull.* 77, 46(1919); *Expt. Sta. Record* 42, 723.—This report deals with the sources of industrial potash in Western Australia and includes descriptions of the uses, manuf., foreign supplies, and local occurrences throughout the State as far as they have been examd. The local sources of potash in Western Australia are wood, seaweed, and coal ashes; feldspar; glauconite; jarosite; and alunite. Chem. analyses of samples of these materials are reported and discussed, with a view to local development. Two appendices, on Examination of Western Australian Seaweeds for Potash and Iodine, by I. H. Boas; and The Alunite Deposits at Kanowna, by T. Blatchford, are also included. H. G.

**Potash and bromine in Texas lakes.** *Am. Fertilizer* 52, No. 8, 72, 73(1920); *Expt. Sta. Record* 43, 127.—It is stated that brines that contain potash and Br have been discovered in alkali lakes in Gaines, Lynn, and Terry Counties, Tex. The sands that form the bottoms of the lakes are impregnated to a depth of from 5 to 20 ft. or more with brine that is composed essentially of the chlorides of Na, Mg, and K. Analyses of samples showed K contents of 3.96 and 4.08%. Analyses made by the U. S. Geological Survey showed KCl contents of 7.51 and 7.78% from the same lakes. H. G.

**Fluorspar and cryolite in 1919.** HUBERT W. DAVIS. U. S. Geol. Survey. *Mineral Resources of U. S., 1919*, Part II, 349-488(preprint No. 25, published July 20, 1921). E. H.

**Graphite in 1919.** L. M. BEACH. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 309-24(preprint No. 22, published July 19, 1921). E. H.

**Patented methods for the production of adhesives.** S. HALEN. *Kunststoffe* 11, 81-3, 90-3, 99-100(1921).—Review of patent's, covering adhesives from starch, sulfate waste liquors, plant constituents, casein, albumin, etc. C. J. WEST

**Carbon as an adsorbent.** R. E. LIESEGANG. *Chem. Ztg* 44, 80-90(1920); *Expt. Sta. Record* 43, 412.—This is a review of the literature on the use of C as an adsorbent



from 1914 to 1919, inclusive. The references are arranged under the headings of the theory of adsorption with C, methods for testing adsorbing properties, prepn. of carbons with strong adsorption properties, applications, and theoretical studies. A list of 44 references to the literature is included.

H. G.

**The casein industry.** J. PEDERSEN. *New Zealand J. Agr.* 19, No. 6, 347-54 (1919); *Expt. Sta. Record* 43, 15.—With a view to obtaining a better quality of com. casein in New Zealand, P. enumerates various causes contributing to poor-quality products and describes in detail several processes of manuf., with their advantages and disadvantages.

H. G.

The manufacture of potash salts as by-products in sugar-cane distilleries (BRIN) 16. Hydrodiffusion of ammonium magnesium sulfate and the separation of the component salts (PORLEZZA) 2.

FRIENDBERG, WILHELM: Die Verwertung der Knochen auf chemischem Wege. Vienna and Leipzig: A. Hartlebens Verlag. 276 pp. M 12.

**Tannic acid from tea.** S. SHIRATORI. Japan 36,577, June 12, 1920. 37.5 kg. tea are treated twice with 270 l. H<sub>2</sub>O at 70-80° for 6 hrs. The ext. is concd. to sirup by evapn., caffeine, etc., is extd. with benzene, and tannic acid is obtained by Et<sub>2</sub>O extn. of the residue.

**Preparation of ammonia by means of a nitrogen compound of silicon and hydrogen.** SEISYŌ MURŌ. Japan 36,767, July 17, 1920. By passing N<sub>2</sub> over a mixt. of 100 parts purified Si and 5 parts pure Fe powder at 1,000-1,200°, Si goes to Si<sub>3</sub>N<sub>4</sub>. When the reaction is completed, the temp. is lowered to 300° and H<sub>2</sub> is passed in, by which means the N combined with Si forms NH<sub>3</sub>.

**Ammonia-saturating apparatus.** T. TŌYAMA AND DENKI KWAGAKU KŌGYŌ CO. (Electrical and Chemical Industrial Co.). Japan 36,557, June 12, 1920. The app. consists of 2 chambers. One contains H<sub>2</sub>SO<sub>4</sub>. NH<sub>3</sub> is blown into this and the reaction product is forced into the other chamber by the pressure of NH<sub>3</sub>.

**Ferrocyanide.** J. SAKAI AND TAKEDA SEIYAKU CO. Japan 36,551, June 26, 1920. 9.4 kg. org. substances containing N, such as waste silk, waste leather or oil cake, etc., 33.75 kg. CaCN<sub>2</sub>, and 7.5 kg. Fe are gradually added to 82.5 kg. fused K<sub>2</sub>CO<sub>3</sub> with agitation. When the reaction is completed, the mass is crushed into small pieces, from which the ferrocyanide is extd. with warm H<sub>2</sub>O at 80° and crystd.

**Separation of calcium salts from brine.** KIKUNAE IKEDA AND TSUNEKICHI NISHIMURA. Japan 36,679, June 30, 1920. In the manuf. of NaCl by evapn. of sea water, CaSO<sub>4</sub> deposits on the inner side of the vessel and reduces its thermal cond. Ca can be almost completely eliminated as CaCO<sub>3</sub> by agitating with powdered MgCO<sub>3</sub>. MgCO<sub>3</sub> or basic Mg carbonate, prepd. by passing CO<sub>2</sub> into a suspension of Mg(OH)<sub>2</sub> in sea water, can be utilized for this purpose.

**Apparatus for production of zinc oxide.** KEITARŌ HIKIYA. Japan 36,640, June 22, 1920. Zn in the state of vapor is brought into contact with hot air, producing fine and homogeneous zinc white.

**Protein from tea-extract residue.** SEMMATSU SHIRATORI. Japan 36,787, July 21, 1920. 37.5 kg. tea are heated with 27 l. H<sub>2</sub>O at 70-80° during 6 hrs. and filtered. 75 kg. residue thus obtained are mixed with 2.6 kg. NaOH and heated at 100° for 1 hr. and filtered. By neutralizing the filtrate with an acid, protein seps. out as brownish scales. The product is tasteless and odorless and is used for prepn. of shellac, varnish and artificial leather, etc.

**Apparatus for reduction of catalyzer.** MINORU MAKI. Japan 36,671, June 30,



1920. A revolving cylinder, capable of being heated, is equipped with agitating and carrying plates; the whole is air-tight. A mixt. of  $\text{NiCO}_3$  and kieselguhr is charged into the drum and the former is reduced to Ni by  $\text{H}_2$ .

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Development of various types of glass. C. J. PADDLE. *J. Soc. Glass Tech.* 4, 299-366(1920).—The prepn., stability, and optical properties of the following series of alkali, PbO, silica glasses were studied:—100  $\text{SiO}_2$ , 40  $\text{Na}_2\text{O}$ , xPbO; 100  $\text{SiO}_2$ , 20  $\text{Na}_2\text{O}$ , xPbO; 100  $\text{SiO}_2$ , 40  $\text{K}_2\text{O}$ , xPbO; 100  $\text{SiO}_2$ , 20  $\text{K}_2\text{O}$ , xPbO; 100  $\text{SiO}_2$ , 20  $\text{Na}_2\text{O}$ , 20  $\text{K}_2\text{O}$ , xPbO; 100  $\text{SiO}_2$ , 10  $\text{Na}_2\text{O}$ , 10  $\text{K}_2\text{O}$ , xPbO, where x varied from 5 to 40 mols. All the glasses can be founded above  $1350^\circ$  and exhibit corrosive action on pot clay, increasing with increased alkali content. Glasses of the soda series tend to devitrify if contg more than 65%  $\text{SiO}_2$ , and those of the mixed alkali series if the silica content exceeds 61%. The potash glasses show no signs of devitrification, but all film badly on prolonged heating at  $900^\circ$ . In all cases density and refractive index increase with increasing content of PbO, the rate of increase falling as the PbO content rises. Dispersion also increases with increase of PbO, but  $\nu$  falls as  $n_D$  rises. Comparison of the above and also of further series contg. equal percentage amts. of potash and soda showed all the soda glasses to have higher densities than the corresponding potash glasses, the mixed alkali glasses having intermediate values. In the equimol. series the potash glasses have slightly higher refractive index and total dispersion, but in the series contg. equal wts. of alkali the soda series has higher refractive index and dispersion. The refractive index and dispersion of the mixed alkali series are intermediate between those of the soda and the potash series. The soly. of the glasses in water decreases as the content of PbO or silica rises but increases rapidly with increase of alkali. Soly. tests prove the following glasses to be of first-class durability for optical requirements:—Glasses of the mol. formulas, 20  $\text{Na}_2\text{O}$ , 30 PbO, 100  $\text{SiO}_2$ ; 20  $\text{Na}_2\text{O}$ , 40 PbO, 100  $\text{SiO}_2$ ; 10  $\text{Na}_2\text{O}$ , 10  $\text{K}_2\text{O}$ , 30 PbO, 100  $\text{SiO}_2$ ; 10  $\text{Na}_2\text{O}$ , 10  $\text{K}_2\text{O}$ , 40 PbO, 100  $\text{SiO}_2$ ; 20  $\text{K}_2\text{O}$ , 40 PbO, 100  $\text{SiO}_2$ ; also glasses of the percentage compns.,  $\text{SiO}_2$  50,  $\text{Na}_2\text{O}$  10, PbO 40;  $\text{SiO}_2$  50,  $\text{K}_2\text{O}$  10, PbO 40;  $\text{SiO}_2$  40,  $\text{Na}_2\text{O}$  10, PbO 50;  $\text{SiO}_2$  40,  $\text{K}_2\text{O}$  10, PbO 50;  $\text{SiO}_2$  60,  $\text{Na}_2\text{O}$  5,  $\text{K}_2\text{O}$  5, PbO 30;  $\text{SiO}_2$  50,  $\text{Na}_2\text{O}$  5,  $\text{K}_2\text{O}$  5, PbO 40;  $\text{SiO}_2$  10,  $\text{Na}_2\text{O}$  5,  $\text{K}_2\text{O}$  5, PbO 50. The first two of the mol. series approximate in optical consts. to well known Schott glasses. The Ben-rath formula 6  $\text{SiO}_2$ , 1  $\text{R}_2\text{O}$ , 1 PbO does not give a very stable type of alkali-PbO-silica glass, a more satisfactory one being 5  $\text{SiO}_2$ , 1  $\text{R}_2\text{O}$ , 1.5 PbO. J. S. C. I.

Rate of change of glass composition following a change in batch composition. J. CURRIE. *J. Soc. Glass Tech.* 4, 382-7(1920).—On changing the compn. of a lime-soda batch supplying a tank furnace so as to increase the lime content of the glass produced, the relationship between capacity of tank, rate of feeding in the fresh batch, and the time taken for the glass worked out to approximate to the desired new compn. was noted. The furnace capacity was 106 tons, the weekly addition of batch 95 to 110 tons (contg. only about  $\frac{1}{4}$  of added cullet from the working end). The change of compn. was not quite complete in 3 months. J. S. C. I.

The theory of the hardening and annealing of glass. J. SALPETER. *Z. tech. Physik* 1, 221-4(1920).—Mathematical expressions are derived for the various strains developed in a sphere of glass as a result of symmetrical cooling from the molten state. It is assumed (1) that the total strain is composed of a plastic and an elastic strain and is compatible with the geometrical shape of the body; (2) that the plastic strain at any



point is the same in all directions, as in the case of a fluid; and (3) that the elastic stresses are everywhere in equilibrium. It is found that the plastic strain is a dilatation at the surface and a compression at the center; that the elastic radial strains are tensions throughout; that the elastic tangential strains are compressions at the surface and tensions near the center; and that the total strain is a radial tension at the surface changing to a radial compression near the center, combined with a tangential compression throughout which is zero at the surface, giving at the center a volume compression and at the surface a volume dilatation. For a certain value of the radius, both the plastic and the elastic volume strains are zero and the density is the same as in the molten state. According to the author, annealing merely changes the elastic strain to plastic, leaving the total strain and density at each point the same as before annealing.

GEORGE V. McCauley

**Influence of silica on the annealing temperature of glass.** S. ENGLISH, F. W. HODKIN, C. M. M. MUTHEAD, AND W. E. S. TURNER. *J. Soc. Glass Tech.* 4, 387-91 (1920).—A series of simple Na silicate glasses ranging from  $2\text{Na}_2\text{O} \cdot 4\text{SiO}_2$  to  $2\text{Na}_2\text{O} \cdot 10\text{SiO}_2$  was examd. The upper annealing temp. was found to rise with increase of silica content, the rate of increase being most rapid between  $2\text{Na}_2\text{O} \cdot 4\text{SiO}_2$  and  $2\text{Na}_2\text{O} \cdot 7\text{SiO}_2$ .

J. S. C. I.

**Melting point of glass; new definition.** F. WEIDERT AND G. BERNDT. *Z. tech. Physik* 1, 121-3 (1920); *Science Abstracts* 24A, 202.—A description is given of a method of defining the m. p. of glass. A cube of the glass is half embedded in kieselguhr with one diagonal vertical, so that the upper half of the cube appears as a square pyramid above the level of the kieselguhr. The cube is then heated to a known temp. for a given time and slowly cooled. The temp. at which the glass has flowed so as to leave just a trace of the apex of the pyramid detectable by touch is only  $20^\circ$  below the temp. required for complete flattening to perfect smoothness in the same time. The mean of these 2 temps. is defined as the m. p. and a table is given for the m. ps. of diff. glasses as found with diff. periods of heating (from  $1\frac{1}{2}$  hr. to 6 hrs.). In the case of a certain flint, the m. ps. for these 2 extreme periods differed by only  $30^\circ$ .

H. G.

**The effects of treating glass surfaces with certain lubricants.** W. SHACKLETON. *Trans. Optical Soc.* 20, 155 (1919); *J. Soc. Glass Tech.* 3, 253.—Tests were made with 3 lubricants, namely, Lasin, Everclear, and Nephelless, in order to det. which was the most effective in preventing "steaming" of the glass surface. The temp. at which the untreated glass was obscured was  $19^\circ$ , and this was reduced to  $-6^\circ$ ,  $-8^\circ$ , and  $-10^\circ$ , resp., after the lubricant had been applied. Nephelless, a prepri. made by S., consisted of glycerol with 20% of Na stearate added.

H. G.

**Progress in manufacturing radio-protective glasses.** W. W. COBLENTZ. *Optician* 58, 265 (1920); *J. Soc. Glass Tech.* 4, 27.—The ideal protective glass absorbed all the ultraviolet and infra-red radiations, and transmitted only visual rays by an amt. sufficient to prevent irritation and injury to the eye. The great demand for colorless optical glass had brought into prominence the coloring effect of Fe impurities. In addition to its visible effect, the presence of Fe caused marked absorption in the infra-red, which reached a max. at  $1\ \mu$ . Transmission curves of six different types of glass were given by C. Colorless glasses showed characteristic absorption bands at  $2.9\ \mu$  and  $2.6\ \mu$ . Window glass gave also the Fe band at  $1.1\ \mu$ . Red glasses were shown to afford no protection against infra-red rays, though all the ultraviolet was absorbed. Amber glass absorbed the ultraviolet and some of the visible. The Fe band was also present. Green glasses were opaque to the ultraviolet, and had the absorption band at  $1.1\ \mu$ . In combination with other glasses they afforded suitable protection from the injurious rays. As cobalt-blue glass absorbed the infra-red, it was largely used in combination with deep amber, red or green glass for protection when working near sources of ultra-



violet radiation. Transmission curves were given of combined red and blue glasses, and of a flashed red, green, and blue set, as such is used in elec. welding, and their suitability for the purpose was thus demonstrated. Curves were also given for two Crookes' glasses, namely, sage-green and blue-green; these were shown to be efficient protectors. Gold leaf on glass eliminated the ultraviolet and infra-red, and with the proper density gave adequate protection from glare by visible rays. The protection afforded by black or smoked glasses was insufficient against ultraviolet rays. "Noviweld," a com. protector, absorbed the ultraviolet and infra-red, but had 10% transmission bands at 2.5, 3.3, and 3.6  $\mu$ . H. G.

**Ultraviolet and visible transmission of various colored glasses.** K. S. GIBSON, E. P. T. TYNDALL, AND H. J. McNICHOLAS. *Bur. Standards, Tech. Papers No. 148*, 27 pp. (1920); *Science Abstracts* 24A, 179; cf. *C. A.* 14, 457.—The paper summarizes investigations on 87 samples of glass, mostly colored. Spectral transmission curves extending from about 710  $\mu$  throughout the visible and ultraviolet as far as any appreciable transmission is evident, are presented. The authors also give a chart connecting thickness of material and transmission. Among the uses to which such glasses may be put are ultraviolet signalling, railway signalling, improvement of visibility (both visual and photographic), eye-protection, selective filters. Photographic, photoelec., and visual methods are described. Photographic detns. were made with the Hilger sector-photometer and a quartz spectrograph. The visual data were obtained mainly with the König-Martens spectrophotometer. In an appendix some particulars of precautions necessary in obtaining data on the ultraviolet region are given and some spectrophotographs showing the effect of various solns. are included. H. G.

**Colored glass batches.** ANON. *Glasind.* 31, 217-8, 225-6, 233-4, 289, 297-8, 305-6 (1920).—Ninety-five batches for colored glasses of many varieties are given. Cf. *C. A.* 15, 154. J. B. PATCH

**Glass cutting.** M. PINK. *Glasind.* 31, 313-4, 321-2, 329-30, 337-8, 345-6, 353-4, 367-73 (1920).—Detailed instructions are given for cutting sheet glass of all kinds, chiefly with the diamond. Cf. Notes on Glass Cutting, *Glass Industry* 2, 90 (1921); *Diamant* 42, 658 (1920). J. B. PATCH

**Gypsum as a substitute for limestone in the glass batch.** R. *Glasind.* 32, 325-6 (1921).—This substitution is not recommended. J. B. PATCH

**The smoke nuisance in glass melting.** LUDWIG SPRINGER. *Glashütte* 51, 355-6, 371-2, 387-8, 403-4 (1921).—A summary of the subject concluded by a personal experience of the author. A glass factory with a 45-m. stack was 150 m. from a forest. Neither  $\text{SO}_2$  nor F-containing compds. were used in the batch. The fuel was coal and briquets in which a later test indicated a content of 2.0 and 1.0% respectively of volatile S. After 6 years of operation damage to the vegetation was evident in the path of the smoke from the stack. No change had been made in the fuel. Analyses of the ash of damaged and unaffected vegetation showed  $\text{SO}_2$  to the extent of 0.19-0.20% in the latter while the former ranged from 0.30 to 0.51%. J. B. PATCH

**The firing of painted glass.** F. HUTH. *Diamant* 40, 43, 57 (1918); *J. Soc. Glass Tech.* 4, 140 (1920).—Every mixture used for glass painting consisted essentially of a coloring substance and a fluxing agent, the latter effecting the combination of the former with the surface layer of the glass during the firing process. These mixts. were divided into two classes: (1) those in which coloring oxides were mixed with the flux immediately before use, and (2) the so-called "glass-painters' fluxes," in which the oxide was already united with the fluxing medium to form a glassy body, this being pulverized and mixed with oil for application to the glass. In order to prevent the furnace gases from coming into contact with the painted glass, the object to be fired was put into a muffle, and this inside the furnace. The muffle might be iron or fireclay, iron muffles



being used for colors which were to be fired at a relatively low temp. The fireclay ensured a more uniform temp. throughout the interior of the muffle, and, therefore, was always used when great heat had to be applied. When the muffle was in the furnace, which might be heated by burning fuel inside it, the temp. was slowly increased, and the easily melted flux and the surface layer of glass combined and took up the coloring oxide. When this was accomplished the temp. must be very slowly lowered or the glass would crack. In practice, test-pieces were put into the muffle with the decorated object, the furnace was run for about three days, and then the test-piece examd. If the firing was complete, the fuel was removed from the furnace, which was closed up and allowed to cool for a further three days before being opened. The firing might have to be repeated two or three times, in which case the second coloring mixt. must contain more flux than the first. The repetition of the firing was a delicate process requiring careful handling.

J. B. PATCH

**The causes of loss in bottles during pasteurization and sterilization.** A. W. BRITTING. *Glass Industry* 2, 171(1921); *Glassworker* 40, No. 39, 21(1921).—Mfrs. reported losses ranging from 0.1 or 0.2 to 3%. The Research Dept. of the Glass Container Association made tests on bottles of various sizes from 4 to 64 ounces capacity. The amount of head space or excess volume over rated capacity was found to vary disproportionately. With the smaller bottles the head space was about 12% of the total capacity, but with the 64-ounce bottles the head space was less than 5%. This extra vol. should be made dependent upon the expansion of the materials used where the containers are to be subjected to heat. The bottles were filled with tap water at a temp. of 60° F. When they were heated to a temp. of 100° the water had expanded 0.7%; 140°, 1.5%; 180°, 2.6%; 190°, 3.0%. The breakage was found to be much less in the case of the small bottles owing not only to the lower pressure generated (because of the relatively larger head space) but also to the fact that small bottles are inherently stronger than large ones. Tap water containing air gave a different result from boiled water. This would indicate a difference in pressure generated between processing cold fruit juices and those which had been previously heated in a kettle. It was recommended that bottles be preheated to 120° F. or more before capping.

J. B. PATCH

**Some calculations of glass technology.** J. B. KRAK. *Glass Industry* 2, 159-60 (1921).—Very clear directions are given for figuring a hatch from a glass analysis and vice versa. A useful table of factors is appended.

J. B. PATCH

**Heat transfer in tanks.** HENRY W. SELDON. *Nat. Glass Budget* 37, No. 10, 1-5(1921).—A discussion of the combustion of producer and coke-oven gases, and of flame temp.

J. B. PATCH

**German sources of silica useful in the glass industry.** HUGO KÜHL. *Glashütte* 51, 340-1, 389(1921).—K. gives 77 locations and analyses.

J. B. PATCH

**New method of setting regenerator chambers.** G. SUCHY. *Sprechsaal* 52, 247(1919); *J. Soc. Glass Tech.* 4, 165-6.—S. continued a discussion on the subject of regenerator chambers in which the checker work was built up on a series of carriages which could be withdrawn and replaced at will. The idea was not new but had never met with general acceptance. In the usual type of furnace—if the dampers were closed during filling-in and correctly regulated during founding, so as to avoid excessive draught—batch dust would not be drawn into the regenerators, and their subsequent stopping up or collapse would be hindered to such an extent that resetting should not be necessary for 1 to 1½ yrs. After this period the regenerators should be reset entirely. In a tank furnace conditions were different. Batch was filled in at hourly intervals and dampers were rarely altered, so that much more batch dust was drawn into the regenerators. The "new" system might be of advantage under these conditions, but as the chambers would have to be reset along their length the process would be very disagree-



able. Glass from the sieve could be prevented from leaking into the regenerators to a great extent by paying particular attention to the covering of the chambers. As the furnace grew older, however, cracks developed, and some glass frequently found a way into the chambers. To avoid this as far as possible, the following procedure was recommended. Before the first pot setting rake over the sieve a dry mixt. of  $\frac{1}{2}$  quartz sand and  $\frac{1}{4}$  plastic clay to fill up all cracks. At each subsequent pot setting fill up all cracks or channels with the same mixt. made into a slip with water, and then cover with a liberal coating of sand. In this way the sieve remained intact, and glass could not leak through. Soft glasses, such as the more fusible lime-soda glasses, could usually be made in furnaces depending chiefly on top heating, but for harder glasses, such as Bohemian crystal, bottom heat was essential. This could be attained by correct furnace practice. For instance, in the improved Siebert furnace, where the regenerators were close under the furnace, so soon as the second filling-in had melted down, the dampers should be lowered. The heat was driven upwards from regenerators and under-furnace, and the flames became clearer, and a steady, successful found resulted. Overflowing from the glass pocket into the chambers could be prevented by closing the pocket with a fireclay stopper luted lightly with fireclay. When the glass pocket became too full, the fluid glass forced out the stopper and flowed into a special pit, thus obviating the arduous work of drawing the glass from the pocket. S. agreed that elliptical regenerator blocks were preferable to the ordinary form, but from experience preferred blocks  $32 \times 10 \times 10$  cm., on the ground that they distributed the heat more uniformly throughout the chambers.

H. G.

**The new method of setting regenerator chambers.** J. BALDERMANN. *Sprechsaal* 52, 363(1919); *J. Soc. Glass Tech.* 4, 166.—B. maintained that the system of setting regenerator chambers by means of movable carriages had proved efficient in practice. For each chamber 3 carriages were necessary, and all 4 chambers could be reset in 2 to 3 hrs., whereas in the case of badly fused chambers it took from 48 to 60 hrs. to put these into good order by the older method. With regard to other points raised in the discussion, the sieve of the furnace could be maintained in much better condition by the use of grog than by using the sand-clay mixt. recommended by Suchy (preceding abstr.), since well burned grog was not so readily attacked by the overflowing glass as were sand and clay, and consequently remained permanent, whereas sand and clay were dissolved by the glass, leaving exposed cracks and channels in the sieve. Further, the pots did not bind so firmly to the sieve when set on coarse grog as when sand is used. In a furnace with top-flame heating it was quite possible to melt a glass contg. 30 parts of soda to 100 parts of sand, or even somewhat harder. The harder the glass the cheaper it was and the better the color. B. pointed out that if the dampers were closed during filling in the result would be that the flame would be driven out through the filling-in holes. He approved the idea of the automatic emptying of the glass pocket, but it remained to be seen whether this would work out well in practice.

H. G.

**The Simplex muffle leer.** C. E. FRAZIER. *Nat. Glass Budget* No. 2, 1(1919 20); *J. Soc. Glass Tech.* 3, 267-9(1919); 2 figs.—The advantages of muffle vs. open leers are enumerated. The Simplex muffle leer is an improvement over other muffle leers owing chiefly to a flat rather than a curved arch. This construction is made possible by use of a cast iron support for the tiles so that each tile has only its own weight to support, reducing breakage and by making thinner walls possible increasing the amount of radiation and thereby the efficiency of the leer.

J. B. PATCH

**The future of ceramic education in America.** EDWARD ORTON, JR. *New Jersey Ceramist* 1, 8(1921).—The author reviews briefly the different systems of ceramic education which are in effect throughout the world. Trade schools in the U. S. have failed to play an important part in our educational system because of peculiar psychol-



logical conditions which prevail. Attempts to combine or to associate closely the trade school and the technical school will fail.

C. W. FARMELER

**Researches in the chemistry of the silicates.** F. M. JÄGER AND H. S. VAN KLOOSTER. *Sprechsaal* 52, 256 (1919); *J. Soc. Glass Tech.* 3, 234-6.—The silicates were prepd. by first heating a mixt. of quartz and the metal carbonate or oxide to the sintering point in an Ir-free Pt dish in an elec. oven, and then completing the fusion in a Fletcher gas furnace. The silicates of Ba, Sr, Be, Zn, and Cd were white and cryst.; that of Zn showed a blue to violet coloring, while those of Mn developed a brown color. In the following table are stated some of the properties of the silicates.  $n_1$  and  $n_2$  are the refractive indices for uniaxial crystals, and  $n_1$ ,  $n_2$ , and  $n_3$  for biaxial. It was found that the meta-silicates have m. ps. which are related linearly to the at. wts. of the metals, the m. ps. rising with increasing at. wts. in the case of Ca, Sr, and Th, and falling with Mg, Zn, and Cd.

Substance.	M. p.	Sp. gr.	Refractive indices.	Special remarks.
BeSiO <sub>4</sub> .....	> 1750°	—	—	—
MgSiO <sub>4</sub> .....	1554°	3.175	$n_1 = 1.641$ ; $n_2 = 1.648$ ; $n_3 = 1.663$ .	—
MgSiO <sub>4</sub> .....	1750°	—	—	—
CaSiO <sub>4</sub> .....	1640°	—	$n_1 = 1.809$ ; $n_2 = 1.850$ .	—
CaSiO <sub>4</sub> .....	2130°	3.27	$n_1 = 1.714$ ; $n_2 = 1.720$ ; $n_3 = 1.737$ .	—
SrSiO <sub>4</sub> .....	1578 ± 1°	3.652	$n_1 = 1.620$ ; $n_2 = 1.580$ .	The melt can be supercooled to 1225° when sudden rise of temp. to 1364° accompanied by crystal takes place. By rapid cooling of the melt, an almost isotropic glass can be obtained with $n = 1.618$ , sp. gr. 3.640, and by careful heating a micro-crystalline variety is obtained.
SrSiO <sub>4</sub> .....	> 1750°	—	—	—
BaSiO <sub>4</sub> .....	1604°	4.435	$n_1 = 1.670$ ; $n_2 = 1.667$ .	Small, weakly double refracting crystals. Attempts to obtain the substance as a glass were unsuccessful.
BaSiO <sub>4</sub> .....	1750°	—	—	—
ZnSiO <sub>4</sub> .....	1437 ± 1°	3.52	$n_1 = 1.623$ ; $n_2 = 1.616$ .	Weakly double refracting crystals.
ZnSiO <sub>4</sub> .....	1609°	—	$n_1 = 1.719$ ; $n_2 = 1.697$ .	Crystals identical with <i>Willemite</i> .
CdSiO <sub>4</sub> .....	1242°	4.928	Both > 1.739.	Crystals with strong double refraction.
CdSiO <sub>4</sub> .....	1252—1243°	—	Both > 1.739.	Crystals with strong double refraction.
MnSiO <sub>4</sub> .....	1273 ± 1°	3.716	$n_1 = 1.739$ ; $n_2 = 1.733$ .	Artificial <i>rhodonite</i> .
MnSiO <sub>4</sub> .....	1290—1300°	4.044	Both > 1.739.	Artificial <i>MnSiO<sub>4</sub></i> has no fixed m. p. Became dark colored on heating through decompo.
CaMg(SiO <sub>3</sub> ) <sub>2</sub> .....	1391°	3.378	$n_1 = 1.654$ ; $n_2 = 1.671$ ; $n_3 = 1.694$ .	—

<sup>1</sup> Observers: Jäger and van Klooster.

<sup>2</sup> Observers: Allen and Wright.

<sup>3</sup> Observers: Day, Allen, White, Shepherd and Wright.

<sup>4</sup> Observers: Jäger and van Klooster.

<sup>5</sup> Observers: Allen and White.

**Contraction of some quaternary (ceramic) mixtures fired to different temperatures.**

H. S. NEWMAN. *Trans. Ceram. Soc.* 19, 132-9 (1919-20).—Slabs were prepd. from ball clay, china clay, stone, and flint in varying proportions, and some of each batch were fired in a saggar to cones 1a, 6a, and 8. Half were then dipped in a lead glaze and half in a leadless glaze and fired to cone 3a. The contraction at cone 016 was less in the leadless glaze and fired to cone 3a. The contraction at cone 016 was less in the majority of cases than the dry contraction, showing that at a certain temp. there is an expansion, probably due to the liberation of combined H<sub>2</sub>O. Until the proportion of stone to flint falls below 3:2 the replacing of ball clay by china clay raises the contraction, and after this proportion is passed the reverse action takes place at the temp. of cone 1a. For cones 6a and 8 the proportion of stone to flint must be below 2:3 before the reversion occurs. The contraction does not always rise with the temp., but with some



mixts. it reaches a max. and then falls again. The gradual substitution of one clay for the other, with the other materials remaining const., does not have a direct bearing on the contraction, nor does the change from stone to flint while keeping the clays const. A large variation can be made in the proportions of ingredients used without affecting the working properties or causing crazing or peeling. J. S. C. I.

The manufacture of architectural terra cotta. L. V. *Rev. mat. constr. trav. pub.* No. 139, 55-57B; No. 140, 70-72(1921).—A history and detailed account of manufl., taken presumably from American literature. LOUIS NAVIAS

Standardization of brick in Germany. ANON. *Rev. mat. constr. trav. pub.* No. 136, 10B(1921).—Building brick are divided into 3 classes: (1) "clinkers" having a compressive strength of 350 kg.; (2) hard-burned brick with a resistance of 250 kg.; (3) building brick of two varieties (a) having a resistance of 150 kg., (b) having a resistance of 100 kg. per sq. cm. Dimensions should be  $25 \times 12 \times 6.5$  cm. If it is impossible to manufl. them this size the relation between length, width, and thickness shall be 4:2:1. The limiting absorption for "clinkers" is 5%, for brick of the 2nd class 8%; the others not detd. All brick should withstand the freezing test. The brick are immersed 25 times in  $H_2O$  and kept at  $-4^\circ$  for periods of 4 hrs. LOUIS NAVIAS

Behavior of clay pyroscopes and fireclay bricks in coal gas. L. BRADSHAW AND W. EMERY. *Gas World* 74, 503-4(1921).—From the Report of the Refractory Materials Research Comm. of the Institution of Gas Engineers. Seger cones, when heated in coal gas to temps. well above their ordinary softening points, remained erect. On examn., they were found to consist merely of a hollow shell with a quantity of slag discharged at the base, or of a semi-vitrified mass covered with an infusible skin. The outer shell was extremely refractory. It appeared to be due to the formation of a thin film of hard carbon in intimate contact with the surface of the cone. This effect was found to be due to the decompn. of  $CH_4$  which forms a peculiarly hard and lustrous type of carbon (cf. Bone and Coward, *C. A.* 2, 3061). Fireclay brick heated under the same conditions assumed a similar surface deposition. The idea of a protective coating of hard carbon artificially produced on fireclay surfaces might possibly be utilized in gas works practice, as the refractoriness of the shell is very much higher than that of the untreated material. J. L. WILEY

Effect of added feldspar on the shrinkage and porosity of aluminous fireclays after being fired at high temperatures. E. M. FIRTH AND W. E. S. TURNER. *J. Soc. Glass Tech.* 4, 392-400(1920).—In a previous paper (*C. A.* 14, 3514) the authors had noted that, of clays which they examn., those of high  $Al_2O_3$  content showed, with two exceptions, the widest range of porosity on firing. It is now shown that if 1 or 2% of feldspar is added to the two exceptional aluminous clays (to act as a flux during firing) the shrinkage is rendered more uniform, and there is a considerable increase of porosity range. J. S. C. I.

Resistance to compression of crude clay bricks and masonry. T. Z. *Rev. mat. constr. trav. pub.* No. 136, 12B(1921).—(Owing to the shortage of coal in Germany, clay bricks in the dry unburned state have been used for building purposes. Tests showed the following resistance to compression: (1) dry brick; (2) after 4 weeks in a moist atm. Column 3 gives the absorption.

	Resistance to compression, Kgs. per sq. cm.		
	(1)	(2)	(3)
Machine made	42.3	27.2	1.09
" "	34.9	21.1	1.02
Hand made	30.9	21.3	1.12
" "	26.1	20.1	0.70

A test made on some pillars composed of 3 to 8 crude brick had a resistance of 9 to 37.1 kg.



per sq. cm. while the resistance of normally burned brick is 150 for 1st quality and 100 for 2nd quality brick.

LOUIS NAVIAS

**Cements for joining refractory bricks.** ANON. *Rev. mat. constr. Iran. pub. No. 136*, 11B(1921).—The effects of various materials on the fusion temp., in cones, of a clay fusing at Cone 30 are given.

% added.	Materials added.					Good fire brick waste
	Portland cement,	Lime.	Asbestos.	NaCl.	SiC.	
0	30	30	30	30	30	30
3	—	—	28-29	—	—	—
4	27	20-26	—	—	—	—
5	—	—	—	26	20	—
6	20	—	19-20	—	—	—
8	19	17-18	—	—	—	—
9	—	—	18-19	—	—	—
10	15	—	—	14	29	—
12	—	11	—	—	—	—
15	—	—	—	5	29	—
16	—	10	—	—	—	—
20	13	—	—	—	29	—
24	—	—	—	—	—	—
25	—	—	—	—	—	30-31
30	11	—	—	—	29	—
40	8	—	—	—	29	—
50	—	—	—	—	29	21

SiC and refractory brick maintained the refractoriness—the other materials lowered it considerably.

LOUIS NAVIAS

**Porcelain.** A. V. BLESINGER. *New Jersey Ceramist* 1, 17(1921).—A general discussion of different types of porcelain, the changes which take place in the firing of such bodies and a few of the defects of such wares.

C. W. PARMELEE

**Investigation of the cause of "blowers" in solid porcelain sanitary ware and the cure.** R. H. MINTON. *New Jersey Ceramist* 1, 27(1921).—The "blowers" manifest themselves by lifting the glaze like fish scales. There are two forms. In one, small particles of quartz or gneiss stones blow off the glaze scales and leave a tiny hole in the center. The second form always shows a black center. The cause of the latter is FeS<sub>2</sub>, which gives rise to the trouble because of improper methods of firing. Rules for proper burning follow: (1) Allow sufficient time for water-smoking so that all the ware is properly prepd. for oxidation, when that period arrives. (2) When cone 020 is reached, allow time for complete oxidation and continue slow firing up to cone 012. (3) When cone 1 is reached, discontinue firing until the top heat has somewhat settled, and avoid heavy reduction during high fire. (4) A draft gage should be used and the draft kept under 5 mm.

C. W. PARMELEE

**Transparency and refractoriness of porcelain.** T. HERTWIG. *Sprechsaal* 54, 11-12(1921).—Five porcelain mixts. with a firing temp. corresponding to Seger cone 9 (1280°) were prepd. from Zettlitz kaolin, Rörstrand feldspar, Pleystein quartz, calcite, and ZnO. The first, corresponding to the formula, (0.65K<sub>2</sub>O.0.35CaO. ZnO) 2.8Al<sub>2</sub>O<sub>3</sub>.14SiO<sub>2</sub> (acid ratio 1:1.49) had a shrinkage of 12.7% and was transparent. Small dishes with flat lids of normal thickness were cast quite satisfactorily, but very thin lids sank slightly. Two mixts. of the formulas (0.8K<sub>2</sub>O.0.2CaO. ZnO) 2.8Al<sub>2</sub>O<sub>3</sub>.17SiO<sub>2</sub> (acid ratio 1:1.8) and (0.8K<sub>2</sub>O.0.2CaO. ZnO) 2.8Al<sub>2</sub>O<sub>3</sub>.18SiO<sub>2</sub> (acid ratio 1:1.91) were not refractory, and similar lids made of them collapsed; this is ascribed to the high content of alkali in conjunction with a high acid ratio. A mixt. of formula (0.83K<sub>2</sub>O.0.17CaO. MgO. FeO).



3.59Al<sub>2</sub>O<sub>3</sub>.16.36SiO<sub>2</sub> (acid ratio 1:1.38) was highly transparent and retained its shape completely at Seger cone 14 (1410°). A mixt. of formula (0.65K<sub>2</sub>O.0.35CaO.MgO.FeO).3Al<sub>2</sub>O<sub>3</sub>.11SiO<sub>2</sub> (acid ratio 1:1.1) was a biscuit mass, with a good mat appearance but of low transparency. The results confirm Dornier's statement (*C. A.* 10, 1416) that excellent porcelain to be fired at Seger cone 9 can be made, but to ensure the ware retaining its shape perfectly, a high K<sub>2</sub>O content must accompany a low acid ratio, and the quartz content must be kept low or the ware will have a greasy appearance. German porcelains are too rich in Al<sub>2</sub>O<sub>3</sub> and quartz and often too low in K<sub>2</sub>O, but if the proportions are altered while ignoring the acid ratio the product will not be sufficiently refractory. A glaze suitable for the first mixt. mentioned above is composed of grog from the same mixt. 22.54%, Rörstrand spar 22.30%, dolomite 9.61%, calcite 7.27%, ZnO 2.05%, calcined Zettlitz (Zebisch) kaolin 8.49%, Pleystein quartz 27.74%, corresponding to (0.2K<sub>2</sub>O.0.2MgO.0.5CaO.0.1ZnO).0.5Al<sub>2</sub>O<sub>3</sub>.4SiO<sub>2</sub>. The inclusion of a little grog increases the adhesion of the glaze and the ZnO increases its whiteness. No raw clay is needed.

J. S. C. I.

A new method of coating pearl beads. O. PARKERT. *Sprechsaal* 52, 23, 191 (1919); *J. Soc. Glass Tech.* 4, 25 6.—Older methods of coating "pearl" beads were unsatisfactory on account of the ease with which the coating was rubbed off. Better results were obtained by coating the beads with hard varnish contg. the "fish silver," but the surface lacked the brilliance of the fire-polished glass. The present process suggested a method for producing the coating on the inside of the beads, thus being protected from abrasion. In the new method, a soln. was prepd. from dry "fish silver," copal varnish, mastic and acetone, possessing the property of rapid drying. The crystal glass beads were cleaned thoroughly with soda and dried. They were then placed in a glass bowl, so arranged and mounted that it could be rotated rapidly about an inclined axis. A portion of the soln. as above was added, the container closed by a rubber cover, and then rotated. After a short period the interior of the glass "pearls" was found to be coated evenly and regularly with the pearl silver, but the excess soln. was contained in the interior of the beads as drops of liquid. To remove this, the cover of the vessel was taken off and the speed of rotation doubled, the vessel being gently warmed by a small flame. In a short time the liquid was evapd., and the coating adhered firmly to the inside of the beads. Aniline colors and lusters could be applied as interior coatings to beads in a similar manner. *Cl. C. A.* 15, 1976.

H. G.

Note on the formation of blow-holes in earthenware glazes. J. BARLOT AND JH. MARTINET. Univ. of Besançon *Chimie & industrie* 5, 651-2(1921).—The most frequent defects found in the enamel of white panels were due to various impurities (Fe and Cu oxides, dirt from the ovens, etc.) or to excessively large grains in the layer immediately under the enamel. These grains often consist of CaCO<sub>3</sub>, which causes shallow and irregular holes in the surface of the enamel owing to the liberation of CO<sub>2</sub>. Another defect consisted of small, round, funnel-shaped cavities, in the bottom of which could nearly always be found a small black particle. Microchemical analysis showed the presence of S by transformation into CaSO<sub>4</sub>, and also of Fe, which results from the decompn. of FeS<sub>2</sub> into FeS and S.

A. P.-C.

Luster glazes. AXON *Keram. Rundschau* 29, 197(1921).—The proper temp. to produce lusters with naphthalene is 2 cones lower than the softening temp. of the glaze. Hence a glaze maturing at cone 02a and having a softening point between cones 012-019 will take a luster at cones 014-017. If the temp. is too high the glaze will blister and if too low it will not take a luster. Paper, sawdust, tar, etc., can be used in the place of naphthalene to produce the desired reducing atm. This method of luster decoration is employed with those glazes containing reducible oxides like CuO, etc.

H. G. SCHUREHT



**The production of the red-brown salt glaze on stoneware.** W. SCHURN. *Tonind.-Ztg.* 45, 249-50(1921).—When stoneware is fired the ferric iron compds. are changed to the ferrous, imparting a gray color to the body. Considerable care is required to change the gray color under the salt glaze to the desirable red-brown color. After the glaze has been applied the kiln is allowed to cool until the kiln atm. is distinctly oxidizing, then the fire holes are closed to prevent rapid cooling. This oxidizing soaking period changes the gray ferrous iron compounds to the red-brown ferric.

H. G. SCHURECHT

**Locating most favorable composition of body and glaze.** P. H. SWALM. *New Jersey Ceramist* 1, 51(1921).—Each individual manufacturer must study the limitations due to the type of kiln, kind of fuel and method of firing.

C. W. PARMELEE

**Preparation of glazes and enamels.** J. B. SHAW. *New Jersey Ceramist* 1, 52(1921).—Red specks are developed in lead glazes by particles of organic matter such as wood fiber from linings of ball mills, or particles of woody matter from ball clay. Many details of prepn. are discussed.

C. W. PARMELEE

**The new Meurer enamel-spraying process.** ANON. *Sprechsaal* 54, 490-1(1921).—Meurer with the aid of the Schoop patents developed a spray whereby enamel is melted and sprayed on metals, etc. With this spray a white enamel as well as others can be applied without a ground coat. The sprayed enamels are more resistant to blows and sudden temp. changes than the kiln-fired enamels which may be partly due to the fact that they can be applied thinner than the kiln-fired enamels.

H. G. SCHURECHT

**Commercial gas properties (DENK) 21. Regenerating chambers (DENK) 21. A Chapman gas-producer installation (ANON) 21.**

**Black tile.** TATSUZO SHIMOSE. Japan 36,725, July 6, 1920. A mixt. of 60% graphite and 40% fire-proof clay is made to a paste with H<sub>2</sub>O, painted on common tile and fired in a kiln to produce fire-proof black tile.

## 20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILBY

**The physical properties of magnesia cement and magnesia cement compounds.** R. J. ROARK. *Bull. Univ. Wis. Eng. Series* 8, No. 5, 257-331(1917); *Expt. Sta. Record* 43, 282.—This bulletin presents the results of an exptl. study of the physical properties of magnesia cement and magnesia cement compds. and of the factors affecting these properties. An important object of the investigation was the detn. of physical tests which could be relied upon to indicate the suitability or unsuitability of particular cements or compds. for use as flooring material. A description of magnesia cement, its manuf. and uses, is given, together with a summary of the results of chemical investigations.

H. G.

**Concrete mixtures in alkali soils.** C. J. MACKENZIE. *J. Eng. Inst. Canada* 3, No. 4, 176-81(1920); *Expt. Sta. Record* 43, 482.—A historical review of the subject is given, and the details of expts. being conducted in Saskatchewan are outlined, the results of which are to be reported later. These consist of a series of actual field tests of concrete in the form and under conditions found in practice, observations of structures in course of construction in troublesome areas, and chem. and physical lab. tests.

H. G.

**Cork stone.** MEHREN. *Kunststoffe* 11, 73-4(1921).—Patents covering the binding of cork with clay and similar substances are listed.

C. J. WAST



**The limestone deposits of New South Wales.** J. E. CARNE AND L. J. JONES. *N. S. Wales Geol. Survey, Mineral Resources* [25] 1919, 411 pp.; *Expt. Sta. Record* 42, 815.—This report deals in considerable detail with the distribution, nature of occurrence, compn., and characteristics of all the known limestone deposits of New South Wales, and describes the present condition of the lime, cement, and marble industries and the possibilities of their further development. It is stated that limestone is widely distributed in New South Wales, the more important deposits occurring within the central and eastern portions of the State. "The great bulk of the limestones of New South Wales are remarkably low in magnesia contents, and though the occurrence of dolomite as a mineral in veins and ore channels has frequently been noted, the workable deposits of high-magnesia limestones are few." Numerous analyses of samples of limestones are included.  
H. G.

**Lime kilns and lime burning.** RICHARD K. MEADE. *Sugar* 23, 264-6(1921).—The various types of lime kilns are described. A water-jacketed cooling cone gives longer service. Reinforced concrete was used to replace the steel jacket for the kiln with excellent results. Relative values of fuels are summarized: one ton bituminous coal hand-fired 3.5-4 tons lime; one ton coal fired as producer gas burns 3.5-5 tons lime; 1 bbl. oil fires 1-1.75 tons lime; 1 cord wood fires 2.25-2.75 tons lime.

C. H. CHRISTMAN

**Slate dust in asphalt road surface mixtures.** OLIVER BOWLES. *Bur. Mines, Repts. of Investigations* No. 2230, 6 pp.(1921).—An effort to find use for waste discarded at slate quarries is described. Waste was ground to fineness of 80% through 200-mesh. A mixt. was made of asphalt 10, slate dust 13, sand 77%. Compression tests on asphalt bonded briquets showed slate flour superior to port. cement and limestone dust and on standard sheet surface mixt. the slate dust was superior to portland cement but inferior to limestone dust. Elutriation tests indicate that slate flour contains approx. 15-25% more of the fine dust that constitutes effective filler than limestone, trap or port. cement.

C. N. WILEY

**Magnesia plaster.** SHŌZABURŌ MIMURA and ROKUSABURŌ YAMAMOTO. *Japan* 36,733, July 8, 1920. Lower coating: A mixt. of 5% saw dust, 10% asbestos and 40% MgO is made to a paste with 44% MgCl<sub>2</sub> in 2-3% 1h acetate soln. Upper coating: A mixt. of 40% MgO, 5% powdered peanut husks, 10% asbestos and 5% pigment is made to a paste by the same MgCl<sub>2</sub> soln. in Ph acetate soln. The plaster is antiseptic and odorless.

## 21—FUELS, GAS, TAR AND COKE

A. C. FURLONG

**Nature of coal.** J. E. HACKFORD. *Mining and Met.* 1921, No. 169; *Tech. Paper* No. 1038, 63-8; cf. C. A. 15, 1384.—Discussion by W. E. Pratt, D. White, E. De Golyer, R. Thiessen, C. E. Waters.

JEROME ALEXANDER

**The most common fuels and methods for their economical combustion.** FRITZ HOYER. *Glas-Industrie* 31, 429-31, 441-5(1920).—Analyses of 9 typical German steam coals are tabulated and their use under boilers is discussed.

J. B. PATCH

**Natalite and the world's motor fuel position.** ANON. *Louisiana Planter* 66, 316-18(1921).—In the use of alc. as a motor fuel a number of difficulties have arisen. Oxidation to AcOH causes marked pitting. A mixt. of alc. 55%, ether 44.9% and ammonia 0.1% gives a perfect fuel. The vapor pressure is sufficiently high and the ammonia neutralizes any acids formed. The production of alc. from various sources and its conversion into "Natalite" are described.

C. H. CHRISTMAN



**Lignite brick fuel.** ANON. *Rev. mat. constr. trav. pub.* No. 141, 95B(1921).—Lignite brick of av. compn. C 55%, H<sub>2</sub>O 13%, ash 6% and volatile combustibles 26% gives 4800 calories of heat energy. It can be used as fuel for all purposes, and is especially of use for heating *lime kilns*. The large volume of volatile matter continuously removes the CO<sub>2</sub>, and thereby keeps the reaction  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  moving in the direction of the disintegration of the CaCO<sub>3</sub>.

LOUIS NAVIAS

**Researches upon brown coals and lignites.** I. Heat treatment at temperatures below 400° as a possible method of enhancing their fuel values. WILLIAM A. BONE. *Proc. Roy. Soc. (London)* 99A, 236-51(1921).—An investigation of typical lignites and brown coals from Australia, Italy, Canada, and Burma showed that for every such coal there is a definite temp., (usually between 300 and 400°) to which the dry coal can be heated without losing any hydrogen or oils, but with a removal of 8 to 15% of the original (dry) weight in the form of H<sub>2</sub>O and a gas which is mostly CO<sub>2</sub>. The calorific value lost (mostly as CO) is less than 3% of the total, so that the product obtained has a much higher heating value and calorific intensity. B. cales. that the flue gas of a steam boiler can supply the heat necessary for this operation, as well as for drying the raw lignite.

ERNEST W. THIELE

**The carbonization of peat and wood.** B. WÄSER. *Z. angew. Chem.* 34, Aufsatzteil, 51-54(1921).—A review, with many references, of recent literature on the gasification of peat and wood, and related subjects. Among the subjects treated are: the peat resources of Germany; the dewatering of peat; a new acid, *humolic*, obtained from peat water; the use of peat and wood for gas-making; metallurgical uses of peat coke; powdered peat; very small gas plants using wood; the use of reeds and rushes in place of peat.

ERNEST W. THIELE

**Value of mixtures of coke breeze and bituminous coke as fuel for a hand-fired boiler.** JOHN BLIZARD AND JAMES NEIL. *Bur. Mines Repts. Investigations* No. 2244, (1921); *Gas Record* 19, No. 12, 25-7(1921).—Use in domestic furnaces was the object in view. Tests were run with a low-pressure boiler of 32.5 sq. ft. grate area. A fine and a coarse breeze were used, each mixed with an equal weight of Pittsburgh coal. The thermal efficiency of each mixt. was about the same as for Pittsburgh coal; but the fine breeze could be used only at low steaming rates, as a very high draft was needed. The coarse breeze mixt. gave only 35-50% as much smoke as Pittsburgh coal alone; the fine mixt., 70-75% as much. The breeze has a steaming value of about 70% of the Pittsburgh coal. Details of the tests are given.

ERNEST W. THIELE

**Peat in 1919.** K. W. COTTRELL. U. S. Geol. Survey, *Mineral Resources* 1919, pt. 2, pp. [I] + 41-6; *Expt. Sta. Record* 44, 215-6.—This report contains data on the production and use of peat in the United States during 1919. In 1919 almost the entire output of peat was used as a direct fertilizer and for a nitrogenous ingredient of com. fertilizers. This was 31% less in quantity and 28 per cent less in value than that reported in 1918. Peat was also used as fuel, stock food, and a source of ale. H. G.

**The peat resources of Ireland.** P. F. PYRCCELL. (*Gr. Brit.*) Dept. Sci. and Ind. Research, *Fuel Research Bd., Spec. Rept.* 2, 25(1920); *Expt. Sta. Record* 44, 124.—The peat resources of Ireland are described and discussed, with particular reference to their utilization as fuel and for producer work. H. G.

**Control of flue gases in mixed firing.** W. OSTWALD. *Nicht u. Eisen* 40, 546-7 (1920).—The main factors in the interpretation of flue-gas analyses are the quantity of excess O over that theoretically required and the compn. of the fuel. "Free" O may be high owing to incomplete combustion. If the ultimate analysis of the fuel is known, the above two factors, in conjunction with the detn. of the CO<sub>2</sub> and excess O, will suffice for control purposes; but if the compn. of the fuel is not known, then a detn. of the CO content of the gas must be made. If the CO<sub>2</sub> content be a %, CO b, O c, and



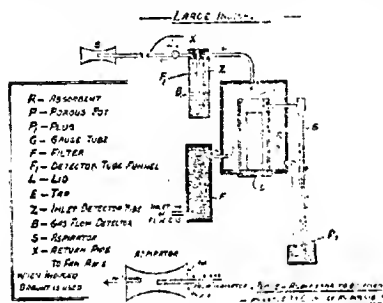
$Nd\%$ , then the C in the flue gases is  $a + b$  (in the gaseous state), the total O is  $a + (b/2) + c$ , while the excess O is  $c - (b/2)$ . With deficiency of air the latter expression is negative, and the two main factors are calcd. as excess air  $= 100[c - (b/2)] / (a + b)$ , and percentage of half-burnt C  $= 100 b / (a + b)$ . Four examples are given to show the application of these formulas to mixed firing. J. S. C. I.

**The recovery of heat from flue gases, and the reheating of air.** ANON. *Rev. mat. const. trav. pub.* No. 136, 6B(1921).

LOUIS NAVIAS

**Scientific control of combustion.** H. T. RINGROSE. *J. Iron and Steel Inst.* (Adv. Copy No. 8), 9 pp.(1921); *Engineering*, 111, 565-6; *Engineer* 131, 511-12; *Iron and Coal Trades Rev.* 102, 628-9.—An app. and a method are described for recording automatically and continuously the amt. of  $CO_2$  in flue gases by measuring on a manometer tube the amt. of vacuum obtained in a porous pot containing a soda-lime absorber and surrounded by an atm. of flue gases, the amt. of vacuum produced depending solely on the  $\%$  of absorbable gas surrounding the pot. It measures very small amts. of  $CO_2$ , even that in ordinary air or about 0.04%.

The quickness or responsiveness of the indication depends solely on the porosity of the pot. The app., as shown in the figure, consists of an aspirator connected to the flue under observation, a filter and a chamber contg. the porous pot, inside which is the dry absorbing reagent. A pipe connects the chamber with a vessel of water, into which dips one end of a graduated tube, the other end being extended into the porous pot. As soon as absorption begins, the vacuum produced and the  $\%$  of  $CO_2$  are read off directly. Another similar app.,



the W. R. Producer  $CO_2$  Indicator, has been devised for measuring the  $CO_2$  in producer gas. For neutralizing the effect of the H another similar pot is provided with a dummy cartridge with no absorbent and H is passed through, setting up in both pots opposing diffusion pressures; the difference in reading on the manometer tube is proportional to the  $\%$  of  $CO_2$  in the mixt. It is accurate to within 0.0-0.05% as compared with an Orsat app. This affords a direct and scientific control of producer gas quality. Attempts are being made to design an instrument so sensitive as to show variations in  $CO_2$  in a water-gas plant from second to second instead of the av. over a certain period. J. I. WILEY

**Regenerating chambers.** F. J. DENK. *Nat. Glass Budget* No. 28, 1; No. 29, 1(1919-20); *J. Soc. Glass Tech.* 3, 263-6(1919); 3 figs.—Regenerating chambers should be so constructed as to abstract as much heat as possible from the waste gases and transfer it to the incoming air and gas, and also to afford easy passage to both incoming and outgoing gases. In connection with the first requirement a series of calcs. was made, and the results were plotted as curves, from which by interpolation all required data could be obtained to det. conditions affecting regeneration. The first series showed the theoretical temp. of combustion of a rich producer gas (30% CO and 4%  $CO_2$ ) for different temps. of the air and an air excess of 25%. The second series showed the influence of the amt. of excess air on the temp. of combustion of a good producer gas (30% CO and 4%  $CO_2$ ) and also on that of a bad producer gas (20% CO and 8%  $CO_2$ ), both gas and air being preheated to 1000° F. In both series the moisture content of the producer gas was assumed to be 50 grains per cu. ft. Although it was found that the actual flame temp. was about 500° F. lower than the theoretical temp. of combustion,



it was considered that other things being equal, the temp. of combustion allowed a fairly accurate estimate of the actual flame temp. to be made. Regeneration was necessary when a producer gas with 25% or less CO was used in order to obtain glass-melting temps. It was not necessary to have a temp. in the regenerators of more than 1500° F., for with 25% excess air and a gas with 25% CO, both gas and air being preheated to 1000° F., the theoretical temp. of combustion would be 3180° F., corresponding to an actual flame temp. of 2700° F. If the percentage of CO were below 25%, a slight increase in the temp. of the regenerator would make up the deficiency in heating value. Producer gas could not be burned in present furnaces without excess of air, but the excess should not exceed 25%. For the efficient working of regenerators it was further recommended that reversals should be made at regular and short intervals; sizes of valves and chambers should be carefully calcd., and the walls of chambers and furnace watched carefully to avoid the presence of cracks and holes. When the most suitable steam pressure has been found for the particular coal available for the producers, it should be strictly adhered to, and there is no reason why the gas should not contain regularly 24–26% CO. Frequent detns. of CO and CO<sub>2</sub> should be made in order that the causes of production of poor gas might be immediately removed. In order to obtain satisfactory heat absorption and transference in the regenerators, it is possible that free passage of gas through the chambers might be seriously hindered with a corresponding decrease in furnace efficiency. The conditions which should in general operate in regard to draft and pressure (in inches of water) in different parts of a furnace are as follows: Gas line, between reversing valve and regenerator +0.6, below regenerator +0.2, above regenerator +0.16, between gas chamber and port +0.28; air line below regenerator -0.04, above regenerator 0000, between air chamber and port +0.12; furnace, above center line very small pressure, on center line 0000, below center line very small draft; flue gas line between port and gas chamber -0.12, between port and air chamber +0.06, above regenerator-gas -0.58, above regenerator-air -0.58, below regenerator-gas -0.76, below regenerator-air -0.72, near stack damper -1.32. (+ indicates pressure, - indicates draft.) The data given are relative, but draft and pressure, respectively, should be found in corresponding points of other furnaces. The reasons for the existence of draft and pressure at various points were given and discussed in detail, and indications given of how those conditions could be used in order to det. the lack of efficiency of a furnace. The causes of fusion in the regenerative chambers were enumerated, and it was emphasized that furnaces should be designed in such a way as to minimize all the possible defects so as to prolong the life of the furnace. J. B. PATCH

**Soot. Origin, properties, and composition.** EVERY NORLIN. *Tekn. Tids., Kem. Berg.* 51, 81–5(1921).—Six kinds of soot are recognized: "fly-soot," free floating particles; "raffelfey," concrement on walls of flues, solid, homogeneous, firmly placed; "scrape soot," like above but porous and easily removed; "fat-soot," concrement of lumps that may run as high as 50% fat; "smear-soot," fly-soot with fat, pitch or tar as binding material; mixed-soot, being a combination of the above. The flash point ranges from 176 (scrape-soot) to more than 400 (fly-soot). Ash is 11% in raffelfey and 47% in fly-soot. The cal. per kg. for fly-soot is less than 4000 [minimum 1800]; the others are in excess of this, over 6000 for smear-soot. Smear-soot may be a less fire risk than the others in that it often carries enough moisture to make ignition impossible. A table also gives: volatile matter, coke, C, H, free acids, sapon. no., benzene ext., acid no., I no., and physical properties of 12 kinds of samples. A. R. ROSE

**Recording ash-pit loss from chain-grate stokers.** E. C. BAILEY. *Mech. Eng.* 43, 381–5(1921); *Elec. Rev.* 78, 967–72(1921).—A device for recording the heat loss from combustible material going to the ash-pit from chain-grate stokers consists of a thermometer bulb filled with N and connected through a capillary Cu tube to a recorder



consisting of a Hg U-tube one leg of which is open to the atm. and carries a float to which the recorder pen is attached. When this bulb is properly located near the rear of a chain-grate stoker, its temp. will respond definitely to changes in the amt. of combustible material going to the ash pit and will vary in direct proportion to the heat thus lost.

LOUIS JORDAN

**The revolving retort; its present status and technical and economic possibilities.** M. DOLCH. *Montan. Rundschau* 13, 117-21, 133-6, 150-1(1921).—The revolving retort ideally fulfills the demands of simple construction, slow rise in temp., production of correct temps. for distg., and easy operation. Coal, lignite and peat are heated successfully in thin layers while in motion, allowing escape of tar vapors, which partially condense in the usual processes, and providing brisker and easier distn. Tar yield is about 90% instead of 60-70% as in generator process. The heat economy is much better than that of the Thyssen oven. Studies of coal in this app. show the presence of abundance of  $H_2$  and lower  $CH_4$  content than reported by Roser. Gas produced from low-quality coals by this process can displace illuminating gas. The coke produced has 80% of the calorific power of the original coal. Comparison of generator and rotary retort plants of the same capacities shows the latter 35% cheaper in cost of operation, higher in conservation of calorific power, more steady in operation, and yielding a gross return of 90% against 49% for the former.

G. R. J.

**Commercial gas properties.** F. J. DENK. *Nat. Glass Budget* 35, No. 34, 1(1920); *J. Soc. Glass Tech.* 5, No. 17, 23-4(1921).—Analyses and data of 12 gases used in U. S. glass factories.

J. B. PATCH.

**The producer for gasification of the natural fuels, with recovery of by-products.** HERMANN KOSCHMIDDER. Berlin-Friedenau. *Brennstoff Chem.* 2, 134-5, 150-2(1921).—The design of producers for wood, peat, lignite and gas-coal is considered. Fuels containing more than about 30%  $H_2O$  cannot be profitably gasified. The height of the producer must take account (a), of a sufficient layer of coke in the lower zone, about 1 m. deep, (b) of sufficient space above this layer so that coal will require 4-5 hrs. to pass through it, wood, peat and lignite 3-4 hrs. For a producer of 2.5 m. diam., this leads to a daily capacity as follows: air-dry wood, 33.3-40.9 (metric) tons; air-dry peat, 47.0-62.7 tons; air-dry lignite, 31.4-47.0 tons; coal, 14.7-19.6 tons, (based on the combustion of 80 kg. per sq. m. per hr. of C in the coke to  $CO$ ). Complete gasification of the fuel for these conditions requires the following heights for the producer: coal, 1.64-1.8 m.; lignite, 2.12-2.76 m.; peat, 4.36-5.00 m., wood, 3.32-3.64 m., exclusive of free space in the top. Requirements for fuel feed, which must be most nearly continuous in the case of the poor fuels of high  $H_2O$  content, and for ash removal and air feed, are discussed briefly, especially the case where a secondary fire at the base of the distn. zone is necessary. The guaranteed efficiencies of com. producers range from 50-65% for wood, peat, etc., to 80% for anthracite, and the weight of fuel required to produce 1 million Cal. in the gas varies correspondingly from 340-670 kg. in the first case to 155-170 in the second. The question of the relative value of the producer and of sep. distn. and gasification cannot yet be clearly answered, being largely dependent on individual conditions.

W. B. V.

**Contributions on the increase of ammonia formation in the distillation of coal. The recovery of hydrocyanic acid in coke-oven gas by transforming it into ammonium sulfate.** FRIEDRICH SOMMER. *Stahl u. Eisen* 41, 852(1921).—HCN may be hydrolyzed by acids or alkalis. With alkalis it behaves as a nitrile giving ammonia and alkaline formate; with acids it is hydrolyzed first to formamide and then further to formic acid and ammonia. The hydrolysis by  $H_2SO_4$  can be used commercially to change the HCN of coke-oven gas to  $(NH_4)_2SO_4$ . The best results are obtained with 60° B $\acute{e}$ . acid and not too high a temp.  $H_2S$  aids the hydrolysis. Expts. are given showing the effect



of impurities and various types of app. on the hydrolysis. The author concludes that\* by making certain additions, which are described, to the scrubbers the HCN can be recovered as  $(\text{NH}_4)_2\text{SO}_4$  without extra expense.

R. S. DEAN

**Thermal losses in the gas-producer process.** N. E. RAMBUSH. *J. Soc. Chem. Ind.* 40, 129-37T(1921); *Iron and Coal Trades Rev.* 102, 870(1921).—Abstr. The factors concerned in the heat losses in the gas-producer process are as follows: (1) The moisture content of the fuel, which is roughly proportional to the thermal loss; (2) the amt. of condensable volatile matter obtained by gasifying the fuel; (3) grading of fuel, when using fuel unevenly graded or in large sizes the depth of the fuel bed must be greater to ensure efficient gasification; (4) dust and soot losses due to high gas velocities and high temps. may represent as much as 3% of the heating value of the fuel; (5) the higher the ash content of the fuel the higher the amt. of unburned carbon; (6) radiation and convection cause a loss of about 1% of the heating value, while the heat loss in the hot ashes is negligible, ranging from 0.1 to 0.5%; (7) gas leakage losses due to poking, cleaning and leaky joints are estd. to be at least 1% of the heating value of the fuel; (8) losses in the cooling and washing plant may cause a loss of 1%; (9) the content of water vapor in the gas, due mainly to undecomposed steam from the blast, depends upon the time factor; (10) the greatest cause of thermal loss is generally the amt. of heat carried away by the hot gases in cold-gas producers but practically negligible in a hot-gas plant. The relative losses with an av. English coal are: in hot-gas producer (if cooled) 17%, cold-gas producer (without recovery) 14.2%, ordinary Mond by-product producer 16.4%. The thermal efficiency of a gas-producer plant is given as 66.3%.

J. L. WILEY

**A Chapman gas-producer installation.** ANON. *Glassworker* 40, No. 44, 11-12 (1921); 3 illus.—A description of the new producer house of the Federal Glass Co. Four automatic feed Chapman Agitator producers are each connected to an 80-ton steel coal bin. The producers are hand-cleaned and the ashes removed by an ash car and track. The electric crane which conveys crushed coal to the bins also loads the ashes into railway cars or trucks as may be desired.

J. B. PATCH

**The determination of benzene hydrocarbons in illuminating and coke-oven gas.** A. KRIEGER. *Z. angew. Chem.* 34, Aufsatzteil, 192(1921).—K. defends the simplicity, rapidity, and accuracy of the Berthold paraffin-oil method for this detn. against the criticisms of Berl, Andress, and Müller (*C. A.* 15, 2167). The latter used far too little wash oil.

ERNEST W. THIELE

**Use of the silent electric discharge for the detection of fire-damp and for gas analysis** (ERLWEIN, BRÜCKER) 7. **Technical gas analysis** (MÖLLER) 7. **New method of setting regenerator chambers** (SUCHV) (BALNEKMAN) 19.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Some chemical considerations of petroleum refining.** BENJAMIN T. BROOKS. *Chem. Met. Eng.* 24, 1022-5(1921).—A plea for more American chemical research in petroleum-refining problems, with publication of results. Among the problems needing attention are the pure chemistry of non-benzenoid hydrocarbons; the refining of unsatd. oils (which are at present unjustly blamed as the cause of bad odor, darkening, and resinification); and the measurement of the lubricating value of oils. ERNEST W. THIELE

**The mines and the refinery of Pechelbronn.** PAUL DE CHAMBRIER AND JACQUES DE CHAMBRIER. *Met. grasses* 13, 5784-92(1921).—A history is given of the development of the refinery and mines of Pechelbronn, together with a geological study of region



and a description of the methods used for working sands for petroleum. Paraffin is refined by refrigeration and decantation. The carbon from the distns. is used to make electrodes. A flow sheet for refining of crude oil is given. R. T. GOODWIN

A comparison of the methods of determining water in petroleum. JERÓNIMO ANGLI. *Anales soc. quim. Argentina* 8, 105-17(1920).—A comparison based on practical tests with a criticism of each method. L. E. GILSON

The determination of water in petroleum. HÉRCULES CORTI. *Anales soc. quim. Argentina* 8, 232-5(1920).—A reply to Angli's criticism of Corti's method. See preceding abstracts. L. E. GILSON

The volatility of internal-combustion engine gasoline. FRANK A. HOWARD. *Sci. Lubrication* 1, No. 2, 14(1921).—Gasoline is defined and volatility is described as its ability to form a stable 1-2% mixture with air. According to the theory advanced complete vaporization of fuels heavier than those now sold is possible. The relationship of time, surface and heat to vaporization is discussed and many tests are cited to bear out the conclusions reached. Many valuable data are given on the physical and chemical properties of internal-combustion engine fuel. D. K. FRENCH

Oil filtration. CARVER WOOD. *Sci. Lubrication* 1, No. 2, 5(1921).—Filtration of lubricating oil is recommended as a means to save power, machinery, time, etc. Several types of filters and their use with various types of engines and machinery are described. Reference is made to the filtration of cutting oil. D. K. FRENCH

Characteristics of Diesel-engine fuels. ANON. *Sci. Lubrication* 1, 13(1921).—A summary of the important points to be considered in the selection of Diesel-engine fuels. D. K. FRENCH

Asphalt and related bitumens in 1919. K. W. COTTRELL. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*. Part II, 279-97 (preprint No. 20, published July 18, 1921). E. H.

## 23—CELLULOSE AND PAPER

A. D. LITTLE

Recent work on constitution of cellulose. C. J. WEST. *Paper* 28, No. 11, 26-7 (1921).—A review of recent articles on the constitution of cellulose. H. H. H.

Hydrolysis of cotton cellulose. GORDON WICKHAM MONIER-WILLIAMS. Whitehall. *J. Chem. Soc.* 119, 803-5(1921).—Ten g. cotton-wool, with 6.93%  $H_2O$  and 0.13% ash, were dissolved in 50 cc. 72%  $H_2SO_4$  and allowed to stand 1 week at room temp. The soln. was then dild. to 5 l. with  $H_2O$  and boiled for 15 hrs. The liquid was neutralized with  $BaCO_3$ , filtered and concd. to dryness. During concn. the liquid was kept neutral to methyl red by addition of 0.1 N  $H_2SO_4$ . The residue was extd. with  $MeOH$ , from which 9.718 g. glucose crystd. 94.5% pure. The yield was therefore 90.67% of the theory. No other products of hydrolysis could be detected. C. J. WEST

The solubility of raw cellulose in ammoniacal copper hydrosulfide and the utilization of this solubility for the valuation of feeding stuffs. F. MACI. *Landw. Vers. Sta.* 91, No. 3-4, 137-55(1918); *Expt. Sta. Record* 43, 315. —This is a discussion of the value of the method described by M. and Lederle (cf. C. A. 12, 2391) for distinguishing between raw and hydrolyzed cellulose by treating the material with ammoniacal  $Cu(OH)_2$  and pptg. the dissolved cellulose with alc. and  $AcOH$ . In addition to the original use of the method, further applications are suggested such as the testing of new feeding stuffs; the quant. detn. of chaff-contg. feeding stuffs; the study of the effect on feeding stuffs and foods of such influences as withering, storage, fermentation, etc.; the study of the relation between raw cellulose and N-free ext.; and the examn. of raw material for textile and paper manuf. H. G.



**Formation of oxalic acid from sulfite cellulose waste liquors and from lignin.** EMIL HÄUSER, H. ROESCH, AND L. GUNKEL. *Cellulosechemie* 2, 13-19(1921).—Lignin free from carbohydrates produced no oxalic acid on fusion with KOH up to 270°; sulfite waste liquors under similar conditions often yield oxalic acid, owing to the presence of cellulose and other carbohydrates in them. Oxidation of lignin with fuming HNO<sub>3</sub> gave yields of oxalic acid up to 25% (20% actually isolated); addition of small quantities of FeSO<sub>4</sub> or Hg<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub> vanadate reduced the yield and the use of a mixt. of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> produced no acid at all, doubtless owing to the destructive action of the H<sub>2</sub>SO<sub>4</sub>. On heating 3 g. lignin with 60 cc. 25% HNO<sub>3</sub> for 4 hrs. at 80-90°, a clear soln. was obtained, from which 0.13 g. oxalic acid was isolated; the yield was increased to over 17% by the addition of 0.01 g. FeSO<sub>4</sub> or Hg<sub>2</sub>SO<sub>4</sub>, but larger amts. of these catalysts acted less favorably.

C. J. WEST

**Paper from bagasse.** ANON. *Paper Makers' Monthly J.* 59, 285, 287, 289, 291 (1921).—Extracts are quoted from *Bulletin* 46, Agr. and Chem. Series, Honolulu, T. H., 1919.

C. J. WEST

**Available supplies of wood pulp.** ANON. *Paper Makers' Monthly J.* 59, 277-9 (1921).—General discussion, giving the acreage, and the consumption of wood for pulp. It appears to be taken from a recent study made in India. In developing the bamboos and savannah grasses, India possesses an important advantage in its own large potential markets for the finished material.

C. J. WEST

**Review of the pulp and paper industry 1919-1920.** C. J. WEST. *Paper Trade J.* 72, No. 26, 44-52(1921).—A review of the technical literature appearing in 1919-1920.

H. H. HARRISON

**Paper-making trials at the Imperial Institute.** C. J. WEST. *Paper* 23, No. 11, 28-31; No. 12, 25-7, 39(1921).—A review of the bulletins of the Imperial Institute at South Kensington describing the paper-making trials on *Andropogon hirtifloris*, *Aninga* stems, Australian bamboo, baobab, black wattle, bourdie grass, *Brachystegia* bark, *Cymbopogon ruprechtii*, *Cymbopogon* sp., *Cyperus alopecuroides*, *Ecdicoclea monostachya* leaves, *Ilibiscus tiliaceus*, Johnson grass, kokerboom, lalang grass, linseed stalks, matai wood, muguguboya bark, niungongo wood, *Neoboutonia macrocalyx*, *Panicum obscurum*, papyrus, rice straw, rice husks, South African grasses, sunflower stems, tobacco brava, Tambookie grass, thatching grass, *Themeda forskalii*, *Trachypogon polymorphus* and *Tristachys rehmanni*.

H. H. HARRISON

**Use of the reed for the manufacture of pulp and paper.** A. KLEIN. *Papier-Zig.* 46, 2043(1921).—While lab. studies indicate that the reed is a suitable material for pulp, the cost of transportation must be considered. One cu. m. of reed gives, at the most, 3 kg. dry bleached pulp. The same vol. of wood gives 120 kg.

C. J. WEST

**Bleaching pulp with liquid chlorine.** E. OFFERMANN. *Papierfabr., Fest- u. Ausland Heft* 1921, 62-5. O. has made a lab. study of the method of de Vains and Peterson (*C. A.* 9, 377) in which the pulp is first bleached with Cl gas and, after washing with alkali, with bleaching powder. The cost varies, as compared with the use of bleaching powder alone, but it averages 60-70% of the older method. O. is of the opinion that the older method might be improved if the process were carried out in steps and the product washed with alkali as an intermediate step. If the liquid-Cl process is put into practice, the question of the formation of hydro- and oxycelluloses must be investigated.

C. J. WEST

**Determining the quality of pulp from its lignin content.** HANS KRULL. *Papierfabr., Fest- u. Ausland Heft* 1921, 65-70.—For Mitscherlich pulp, the following relations are given: 6.5-7% lignin, hard; 5.5-6%, normal; 5-5.5%, soft; 1.0-2.0%, bleached. For Ritter-Kellner pulp: 7.5-9.5% lignin, hard; 6.5-7.5%, normal; 4.5-6.5%, soft.

C. J. WEST



Advances in the utilization of sulfite waste liquor by evaporation using the heat pump. E. WIRTH. *Papierfabr., Fest- u. Ausland Heft* 1921, 70-74. C. J. WEST

Work of the Institut für Cellulosechemie der Technischen Hochschule Darmstadt. EMIL HEUSER. *Papierfabr., Fest- u. Ausland Heft* 1921, 75-81.—General review of recent and present problems. C. J. WEST

Utilization of sulfite waste liquors. LOUIS E. ANDER. *Kunststoffe* 11, 74-7, 88-5(1921).—General review, specially of patents. C. J. WEST

Titration of sulfite liquors. R. SEIBER. *Paper*, Apr. 6, 1921, 24-7.—See C. A. 15, 945. H. G.

Determination of the degree of digestion of sulfite pulp. R. SEIBER. *Paper*, Apr. 6, 1921, 17-22. See C. A. 15, 436. H. G.

New methods for the digestion of plant material. V. POSSANNER. *Papierfabr.* 19, 694(1921).—Review of the patent literature. C. J. WEST

Steam consumption in cooking and drying of sulfite pulp. HARRY ALFTHAN. *Papierfabr.* 19, 657-9(1921).—The steam consumption for bleaching pulp is found to be 1808 kg. per ton air-dry pulp, that for hard pulp, 1944 kg. per ton. The expt. was carried out during the winter months. C. J. WEST

Testing the absorptive capacity of spinning paper for moisture. FR. HERIG. *Papierfabr., Fest- u. Ausland Heft* 1921, 32-4.—Finely powdered aniline dyes (mahogany red is best but methyl violet is also satisfactory) are sprinkled over the paper (an app. is described for arranging this dye in the form of a figure) and the paper is floated on water. When the water penetrates to the dye, the time is taken. Various samples vary in time of penetration from 9 to 123 sec. C. J. WEST

The grasses of the Eastern Coast Belt available for the manufacture of paper, and the possibilities and prospects of paper making in the Union of South Africa. C. F. JURITZ. [*Union S. Africa, Min. Mines and Ind.*] *Ind. Bull. Ser.* 1919, No. 7, pp. IV+115; *Expt. Sta. Record* 43, 317.—This bulletin consists of reports of an investigation of the paper-making possibilities of various grasses of the Eastern Coast Belt of South Africa and of the com. prospects for such an industry. H. G.

German cigaret papers. W. HERZBERG. *Papierfabr., Fest- u. Ausland Heft* 1921, 35-8.—The results of the investigation of 1 French and 2 German cigaret papers are given (color, thickness, weight, tearing strength, ash content, fiber compn., porosity, etc.). H. concludes that German paper today is better than French paper before the war. C. J. WEST

Sizing paper with colloidal rosin. F. STÖCKIGT AND A. KLINGNER. *Papierfabr., Fest- u. Ausland Heft* 1921, 50-60.—It is possible to size paper advantageously with colloidal rosin, but only by the use of  $Al_2(SO_4)_3$  as electrolyte. The sizing process appears to take place in two phases. The 1st is the formation of an adsorption compd. of rosin and Al hydroxide and the 2nd the adsorption of this colloidal phase by the fibers. The difficulties of sapon. of pine rosin are lacking in the use of colloidal rosin. One can, by the use of the same amt. of pine rosin, secure the same degree of sizing as with colophony. The following physical and chem. constants of colophony and pine rosin are given: Moisture, 0.32, 1.32; sp. gr., 1.084, 1.19; m. p., 83°, 80°; ash, 0.71, 0.65%; insol. in petrol. ether, 4.9, 53.9%; acid no., 175.5, 119.6; sapon. no., 184.6, 133.6; ester no., 9.1, 14; rosin no., 72.53, 117.3; 0.25 g. of pine rosin dissolves in 1 cc. alc. at 50°, 0.09 g. at room temp. C. J. WEST

By-products in wood-pulp manufacture. ANON. *Paper Makers' Monthly J.* 59, 269(1921).—Discussion of Rimman's process, in which the black liquor is evapd. to 35° Bé at 60°, a carefully calcd. quantity of NaOH added, together with  $Ca(OH)_2$  or CaO, and the mixt. distd. in a closed retort at not over 500°. The by-products from 1,000 lbs. pulp are: MeOH, 22 lbs.; acetone, 22 lbs.; light oils, 44 lbs.; heavy oils (b. p.



150°), 88 lbs. From grasses and cereal straws the yield of MeOH is about half the above.

C. J. WEST

**Paper-pulp supplies from India.** WM. RAITT. *Paper Makers' Monthly J.* 59, 227-30(1921); cf. C. A. 15, 2723.—R. points out the value of bamboo as a paper material and believes that chem. bamboo pulp can be prepd. to compete with mechanical pulp.

C. J. WEST

**Bamboo by-products.** SINDALL AND BACON. *Paper Makers' Monthly J.* 59, 189, 191(1921).—A discussion of the Rinman process as applied to bamboo waste liquor. The estd. by-products based on a 10,000 tons air-dry pulp mill, are: MeOH, 388,000 kg.; acetone, 330,000 kg.; ethyl methyl ketone, 220,000 kg.; light oil (gasoline), 220,000 kg.; heavy oils (Diesel engine), 572,000 kg. These amt. to nearly 10% calcd. on the original raw bamboo.

C. J. WEST

**The testing of wood pulps.** G. H. GEMMELL. *Pulp and Paper Mag. Can.* 19, 555-7(1921).—See C. A. 15, 314.

H. H. HARRISON

**Determination of ground wood pulp.** C. J. WEST. *Paper* 28, No. 10, 33(1921).—Ground wood can be detd. by the zinc chloriodide and aniline sulfate color reaction, by the action of phloroglucinol upon the lignin of the wood fibers or by the use of *p*-nitroaniline as a quant. reagent.

H. H. HARRISON

**Sulfite tests of average wood, infected wood and chipper dust.** JOHN S. BATES. *Pulp and Paper Mag. Can.* 19, 607-10(1921).—Mill tests, on infected wood gave yields practically the same as for av. wood and showed that infected wood is still good for sulfite, provided that decay has only discolored the wood without reducing it to soft punk. Chipper sawdust cooked under milder conditions than are customarily used with av. wood produced a pulp dirtier than usual but comparatively good in color and general appearance.

H. H. HARRISON

**Purification of viscose.** KÔJIN MINAMINO. Japan 36,666, June 29, 1920. Through viscose in a revolving drum, 0.1%  $\text{NH}_3$  is passed. Then  $\text{SO}_2$  is passed in for 3-4 hrs. at 2-3 lbs. per sq. in., while the drum is rotated at the rate of 10-20 r. p. m.  $\text{SO}_2$  acts on free NaOH, yielding  $\text{Na}_2\text{SO}_3$  and as a bleaching agent.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**Miscellaneous investigations of primer and detonator compositions.** A. LANGHANS. *Z. ges. Schiess-Sprengstoffw.* 16, 41-3(1921).—(1) It was found possible to identify and roughly estimate  $\text{Hg}(\text{ONC})_2$  in primer or detonator comps. by microscopic examn., (250-400 d.), even after such mixts. had been loaded and pressed. (2) In detn. of moisture in comps. contg. S, a temp. of 100° causes sublimation of S. (3) Calcd. values for temp. of explosion, gas vol., and calories evolved on explosion are shown for  $\text{Hg}(\text{ONC})_2$  alone and mixed in various mol. proportions with  $\text{KClO}_3$ . (4) Zn and Pb foil were investigated as substitutes for Sn foil disks for covering primers. Both were attacked and became coated with globules of Hg. (5) Substitutes for  $\text{Sb}_2\text{S}_3$  were investigated. Realgar caused clogging of loading app., gave  $\text{As}_2\text{O}_3$  fumes on firing, and reacted readily with fulminate in presence of moisture, developing acidity. Sulfides of Fe, Zn, and Cu were tried with indifferent results. Among numerous fused mixts. of  $\text{Sb}_2\text{S}_3$  with other sulfides, 1 part  $\text{Sb}_2\text{S}_3$  + 3 parts  $\text{Cu}_2\text{S}$  gave the best results. (6) Blasting caps prepd. with the fulminate in intimate mixt. with TNT, instead of in a superimposed layer, gave const. failures; the mixt. either was not ignited or burned without explosion. Other caps were tried with a layer of fulminate on top of a mixt.



of 4 parts  $\text{KClO}_3$  and 1 part S, or a mixt. of  $\text{KClO}_3$  and  $\text{Sb}_2\text{S}_3$ . These detonated, but without sufficient strength to perforate lead plates. C. G. STORM

**Military detonators and peaceful industries.** PAUL GALEWSKY. Dresden. Z. ges. Schiess-Sprengstoffw. 15, 153-4, 163-4, 190-1, 197-9, 203-4, 212-14(1920).—The av. monthly requirements of the German Army during the war amounted to 20 million detonators of 20 different grades and types, 400-500 million primers of 40 varieties, and 2000 km. of fuse of 3 main varieties. The difficulties of supplying these requirements are discussed. 20 million detonators of  $\text{Hg}(\text{ONC})_2$  required 45 t. of Hg per mo., while the supply was only 10 t. For the manuf. of the fulminate was also required 4,050 t. potatoes (for manuf. of alcohol), and 450 t.  $\text{HNO}_3$ . In 1917 lack of these raw materials forced the replacement of fulminate by tetryl in every grade of detonator; e. g., the charge of 2 g.  $\text{Hg}(\text{ONC})_2$  in No. 8 detonators was replaced by 0.8 g. tetryl or TNT+0.5 g.  $\text{Hg}(\text{ONC})_2$  or 0.85 g. tetryl+0.25 g.  $\text{PbN}_6$ +0.25  $\text{Pb}(\text{CNS})_2$ . The Cu for detonator shells was substituted first by Zn, then by Fe, and finally by Al. Although further developments were stopped by the armistice, Al was found highly suitable for detonator shells not contg.  $\text{Hg}(\text{ONC})_2$ , and also for the manuf. of primer cups. Paper coated with asphalt, bakelite, etc., was substituted for metal foil for covering cap compositions. Cotton and jute threads in safety fuse were replaced by paper yarn. Among commercial developments predicted are the general use of Al for the manuf. of blasting cap shells and primer cups, and the replacement of fulminate in detonators by such explosives as TNT, tetryl and  $\text{PbN}_6$ . C. G. STORM

**Matches.** SAKUSHIRÔ HATAKEYAMA AND CHÔJI FUNAI. Japan 36,814, July 24, 1920. A mixt. of 5 g. special ppt., 12 g.  $\text{KClO}_3$ , 0.1 g. S, glue and  $\text{H}_2\text{O}$  is used as striking head; while a mixt. of 1 g. red P, 1 g.  $\text{SnO}$ , glue and  $\text{H}_2\text{O}$  is painted on the box. The special ppt. is prepd. as follows: 162 g. cellulose are mixed with 80 g. NaOH and 500 g.  $\text{H}_2\text{O}$ , and 249 g.  $\text{CuSO}_4$  are added after 1 hr. The larger part of cellulose is dissolved by careful addition of  $\text{NH}_4\text{OH}$  and filtered by suction. To the filtrate, 16 g.  $\text{K}_2\text{Cr}_2\text{O}_7$  are added, and the special ppt. is produced by adding Pb acetate soln. Cf. C. A. 15, 1402.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**Dyes for linoleum.** FELIX FRITZ. *Kunststoffe* 11, 89-90(1921).—The requirements are discussed and some of the suitable dyes are listed. C. J. WEST

**Colors from naphthol with *o,o'*-dihydroxydiazobase.** F. BLUMER. *Bull. soc. ind. Mulhouse* 87, 47-50(1921).—Solns. of diazonium salts treated in a slightly alk. medium with ring compds. containing  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$  or halogens, couple with the product containing OH ortho to  $-\text{N}=\text{N}-$ . The resulting dyes are sol. in water and because of their acid properties are applicable to wool. This paper reports studies upon analogous but insol. dyes applied to cotton. On coupling the diazo compds. of the following named amines in a slightly acid medium with naphtholated fiber, orange to red azo colors were produced; in a slightly alk. medium the azo color varied from violet to blue: 2,3-dinitroaniline, 2,4-dinitroaniline, tribromoaniline, 1,6-dibromo-4-nitroaniline, 2-bromo-6-nitro-*p*-toluidine. Picramic acid and 2,6-dinitro-*p*-toluidine coupled with difficulty. The work of Brenner (cf. C. A. 14, 1271) is applied in this study.

L. W. RIGGS

**Zero water in wool dyeing.** HOWARD L. TIGER. *Textile World* 60, 685, 689(1921).—In answer to an inquiry regarding the benefits of zero  $\text{H}_2\text{O}$  in dyeing, T. points out



the losses and difficulties in dyeing due to the use of hard water and how they can be avoided by zeolite softening. Four photomicrographic illustrations. C. E. M.

**Freihurger process for discharging nitric acid.** CHARLES SUNDER. *Bull. soc. ind. Mulhouse* 87, 51-4 (1921).—The faults and limitations of Freiburger's first app. for passing cotton goods through rather concd.  $H_2SO_4$  at  $60^\circ$  B $\acute{e}$  are described, also the mechanical improvements suggested by Solbach. To avoid some of these difficulties a portion of the nitrate is replaced by nitrite. After a careful review of the process, S. states that its advantages are less than appear at first sight. Before adoption of the process a careful calcn. should be made as to the economy of a number of factors which vary according to the case.

L. W. RIGGS

**Cellonia seefflaehs.** CAMILLO PERTUSI. *Prog. ind. tessile tintorie* 1920, No. 4; *Giorn. chim. ind. applicata* 2, 399-400 (1920).—Cellonia seefflaehs is the name of a fibrous material recently put upon the market. It is rather rough to the touch and is composed of fragile filaments of a light ashy color. The filaments are 4-12 cms. long, av. = 7 cm., 0.026-0.090 mm. thick, av. = 0.070 mm., and are made up of fibrils which, under the microscope, recall the fibrils of jute. The substance is difficultly attackable by  $58^\circ$  B $\acute{e}$   $H_2SO_4$ , and resists well 10% KOH even after 15 min. boiling. The fiber and the soln. take on an orange-yellow color. Fuming  $HNO_3$  immediately colors it dark maroon red; if the action is continued for 1 min., the filaments become transparent and are resolved into the elementary fibers. It does not color blue with I and  $H_2SO_4$  even after treatment with 10% KOH, indicating a strong lignification. It is insol. in Sweitzer's reagent. It contains 1.6% of fatty substance extractable with  $CCl_4$ , 3% ash, and 11.9% hygroscopic  $H_2O$ . The tensile strength of the fiber is low. A thread of number 4 (international classification) resists a breaking force of only 700 g.

R. S. P.

**Use of glue in wool handling.** LUIGI RINOLDI. *Prog. ind. tessile tintorie* 1920, No. 2; *Giorn. chim. ind. applicata* 2, 400 (1920).—From his expts., R. obtained the following results. Glue increases the deterative power of soda and of soap in degreasing wool, hinders or reduces to a minimum the soly. of wool in these baths. The greater yield (4-5%) in washed wool compensates for the greater cost due to the glue. Glue operates as an equalizing and penetrating medium in dyeing with acid colors. It obviates the addition of  $Na_2SO_3$  and saves the fiber, the soly. of which becomes less evident in the bath. It increases the dynamometric resistance of the fiber. Glue accelerates the operation of felting, produces a smaller quantity of burrs, gives greater wt., and a better feel to the cloth.

ROBERT S. POSMONTIER

**Carbonizing raw stock and piece goods.** FREDERICK ALBERT HAYES. *Textile World* 59, 3937-9, 4167-9 (1921).—A general description of the  $Al_2Cl_3$  and  $H_2SO_4$  processes.

CHAS. F. MULLIN

**"Friction marks" on dyed cotton goods.** EDWARD O. HOLMES, JR. *Textile World* 59, 4171-3 (1921).—Expts. proved that marks appearing upon S-dyed khaki cloth were caused by rubbing the wet cloth before dyeing.

CHAS. E. MULLIN

**Extraction of soaps and oils from silks.** H. S. MUDGE. *Textile World* 60, 583 (1921).—The results are given of lab. work to det. the best solvent and working conditions for the estn. of oil and soap in thrown silk. Soxhlet extrns. gave results as follows with soft gum and yellow Japan, and Canton hard gum silks: Alcs. change during the extrn.; the Cl of chlorinated solvents ( $CCl_4$ ,  $CHCl_3$ ,  $C_2H_5Cl$ , or  $C_2H_4Cl_2$ ) unites with the silk even in the presence of MeOH or AmOH. This Cl is non-volatile at  $140^\circ$  but is removed by the boiling-off operation;  $Et_2O$  and  $CS_2$  are regarded as too flammable;  $CCl_4$  has too high a b. p.; freshly distd. petr. ether 3 or 4 parts with 1 part MeOH works well; acetone is perhaps best of all the solvents tried, and only about 6 siphonings are necessary or advisable. A little alc. may be added to the acetone, if desired, to increase the solubility of soap. About 0.3% is extd. from the silk itself, which may be used as



a correction factor. Most of the solvents tried unite with the silk, giving a greater wt. to the extd. silk than the original sample, therefore the non-volatile residue of the solvent must be weighed. Care must be exercised in weighing the dried silk sample on account of its hygroscopic nature. Two tables of results are given. CHAS. E. MULLIN

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The color of the indigoids (MARTINET) 10.

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Imitation hemp fiber. SHIGE TAKASU AND YOKOHAMA KÔGYÔ Co. Japan 36,743, July 16, 1920. Cotton threads are immersed in dil. Al acetate soln., squeezed and dried at low temp. They are subsequently treated with a mixt. of 100 parts viscose soln. from vegetable cellulose, 10 parts resin soap and 5 parts Turkey red oil, dried, steamed for 1 hr., washed and dried. The product can be washed, dyed and bleached.

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## 26—PAINTS, VARNISHES AND RESINS

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A. H. SABIN

Thickness of wet paint films. A. H. PFUND. Johns Hopkins Univ. *J. Franklin Inst.* 191, 517-23(1921).—A new app., the "Paint Film Gauge," has been devised to measure the thickness of films of wet paint; the accuracy attainable is better than 3%. The app. consists of a convex lens whose lower surface has a radius of curvature of 25 cm., it is mounted at the bottom of a short tube, *T*, which slides freely in an outer tube. Compression springs keep the convex surface out of contact with the paint film until pressure is applied at the top of *T*. The app. is simply rested on a painted surface; and the lens is forced down as far as it will go. "Upon releasing the pressure before removing the gauge, a circular spot is left on the gauge as well as on the painted surface. The diameter of the spot on the gauge is measured to 0.1 mm. If the spot is elliptical, the mean of the major and minor axes is detd. A series of readings on at least 10 spots, judiciously distributed over a given area, yields a fair value of the av. thickness of film." By reference to a table, from the diam. of the paint spot on the lens, both the thickness of the paint film in mm., and the number of sq. ft. of surface covered by 1 gal. of the paint may be read directly. Study of various types of paint showed that variations introduced by painters are greater than those introduced by the paints. In actual practice, spreading-rate was not a const. for a given type of paint. The hiding power of paints, especially those which become markedly brighter on drying, increased as brightness increased, and was but little affected by shrinkage of the paint film during drying. JOSEPH S. HEPBURN

The manufacture of ink. BRUNO WALTHER. *Chem.-Ztg.* 45, 430-2(1921).—A brief review of the compn. and physical and chem. testing of Fe gallate, logwood ext., copying, hectograph, lithograph, stamping and marking inks; with formulas, methods of manuf., specifications, etc. F. A. WERTZ

Notes on varnish cooking. MANFRED RAGO. *Farben-Ztg.* 26, 2335-6(1921).—R. suggests that the "running" of a gum and the subsequent incorporation of a drying oil with it, forms more than a mere soln. of gum in oil; and points out the possibility of the formation of resin glycerides with liberation of an equiv. amt. of fatty acids. His lab. expts. made with rosin and linseed oil indicate, however, that no appreciable quantities of fatty acids are set free as a result of exchange of the glycerol radical with the abietic acid. When a metallic acetate such as Pb, Mn, Co, is heated with linseed oil or rosin, the AcOH radical is not volatilized as is generally supposed, but a large part of it remains, probably as part of a newly formed complex compd. such as a Pb aceto-



abietate. In similar manner, linseed oil varnishes might be glycerides of a hypothetical linolic-resin acid.

**Notes on analysis of oil varnishes.** H. WOLFF. *Farben-Ztg.* 26, 2208-9(1921).—W. reviews the method of deWaele (*Chem. Umschau* 28, 83(1921)) for the analysis of varnishes, and believes it to be the best published; but suggests certain modifications. Esterification by the Wolff method (*C. A.* 8, 2495) instead of by the Twitchell method saves considerable time, and examn. of the sepd. fatty acids gives an indication as to whether tung oil is present. Petroleum ether will dissolve considerable proportions of certain copal resin acids, so that deWaele's method of sepg. copal from rosin acids may lead to erroneous results which will depend on the character of the resin, on the "gum" melting process used in making the varnish, etc. The Lieberman-Storch color reaction for detecting dammar is not reliable. Analyses of oil varnishes should show as far as possible, definite isolated compds. such as abietic acid; or should state minimum quantities of resin present rather than give results obtained by calcn. by the use of arbitrary correction factors. For the sepn. of fatty and resin acids, extn. with a variety of solvents is often useful. Information on the form in which rosin acids occur can sometimes be obtained by first removing from the varnish the fatty and resin acids which are present as free acids or as metallic salts such as Ca resinate, metallic driers, etc. The unsapon. matter is next extd., and if appreciable quantities of abietic acid still remain in the sapon. mixture, then it is reasonably certain that rosin was present as ester gum.

F. A. WERTZ

**The alcoholysis of balsams.** ERNEST FOURNEAU AND MARIO CRESPO. *Analges spec. espagn. fis. quim.* 18, 148-53(1920).—The balsam is boiled, a reflux condenser being used for 6 hrs. with an equal wt. or more of 95% EtOH containing 3% of HCl gas. The mixt. is then distd. with steam and the esters are extd. from the distillate by ether and separated by fractional distn. in vacuum. All of the benzoic and cinnamic acids both free and combined in the balsam may be thus isolated as their ethyl esters. The benzyl alc. is resinified and remains in the non-volatile residue. However, if EtOH *sold.* with HCl be used some benzyl chloride is formed and distills over.

F. A. WERTZ

L. E. GILSON

**Properties and reactions of the resin of Euphorbia dendroides.** M. GIUA. *Ann. chim. sci. ind.* 37, 80-83(1921).—The milk of *Euphorbia dendroides* (widespread in North Italy) was dissolved in ether and the solvent again evapd. to prevent coagulation. It does not contain any N; with  $\text{H}_2\text{SO}_4$  it turns dark red; this color is intensified by addition of  $\text{K}_2\text{Cr}_2\text{O}_7$ . Characteristic is the reaction of Liebermann-Burchard with  $\text{CHCl}_3$  and  $\text{Ac}_2\text{O}$ , resulting in a red coloration. Chromate soln. is reduced. The milk of *Euphorbia cyparissias* has the same reactions;  $d_{20}^{20}$  1.0722.

E. FIERTZ

**Dyes for linoleum (FRITZ) 25.** The action of inks on metallic iron (BAUER, MRECK-LENBURG) 9.

## 27—FATS, FATTY OILS AND SOAPS

H. SCHERUBEL

**Progress in fat chemistry in 1918.** W. FARRION. *Chem. Umschau Fette, Ole, Wachs, Harze* 26, 197-9, 209-11, 221-3(1919); *Expt. Sta. Record* 43, 201.—This is a review of the literature on theoretical, analytical, and technical fat chemistry. H. G.

**Report by the Committee of Analysts on standards of good merchantable quality.** O. HENNER, *et al.* *Analyst* 45, 286-9(1920); *Expt. Sta. Record* 44, 413.—This report presents in tabular form schedules of standards for vegetable oils, seeds, nuts, and kernels of good merchantable quality. The standards for oil include percentages of free fatty



acids calcd. as oleic, moisture, and unsaponifiable matter, and certain other standards in individual cases. The standards for seeds, nuts, and kernels consist of the oil content and percentage of free fatty acids in the extd. oil. H. G.

**Report by the Committee of Analysts on standard methods of analysis of seeds, nuts and kernels, fats and oils, and fatty residues.** O. HEHNER, *et al.* *Analyst* **45**, 278-86(1920); *Expt. Sta. Record* **44**, 412-3.—This report of the committee appointed in November, 1918, by the Director of Oils and Fats (England) to consider the settlement of standard methods of analysis of oil seeds, fats, and oils, consists of detailed methods for the detn. of oil in seeds, nuts, and kernels; for the various analytical consts. of oils and fats; and for the evaluation of fatty residues such as soap stock, acid oils and fatty acids, cottonseed oil, black grease, and mucilage. H. G.

**Esterized fatty acids.** J. WOLFF, Lab. of the S. H. and V. Ges. *Z. deut. Oel-Fett-Ind.* **41**, 323-4(1921).—In 1919 the soap syndicate of the Imp. Com. received offers of esterized fatty acids, presumably of Hollandish origin. Analysis showed them to be mixts. of coconut oil with moderate amts. of ethyl esters of the fatty acids and the conclusion was drawn that an unsuccessful attempt had been made to convert a low-grade coconut oil into an edible product by esterizing it with grain alc. The analytical methods are described, consisting of saponifying and acidifying the fat under a reflux condenser, distg. off the ethyl alc. and detg. the glycerol in the residual acid water (the dichromate method gave 1.3-3.9% higher results than the acetin method) and detg. the usual consts. of the fatty acids. An unsuccessful attempt was made also to sep. the ethyl esters from the coconut oil by sapon. with  $\text{Na}_2\text{CO}_3$ , but after acidification of the product, acid nos. of only 3.7-7.4 were found. P. ESCHER

**Detection and estimation of illipe butter used as substitute for cacao butter.** FRANCIS G. H. TATE AND JOHN W. POOLEY. *Analyst* **46**, 229-36(1921).—T. and P. have developed a method for the detn. of illipe butter in the presence of cacao butter. A "factor" for each butter is obtained by multiplying the av. values of  $d_{15.5}^{20}$ ,  $d_{15.5}^{25}$ , viscosity, m. p., m. p. of the fatty acids, and the reciprocal of I no. (Wijs) for each fat. They are, for cacao butter, 3150; and for illipe butter, 4403. From these consts. the percentage of each fat in a mixt. can be calcd. These consts. cause an error in the calcn. which T. and P. detd. exptly. A table of corrections is given. A "short factor" for use when a limited amt. of sample is available is calcd. from m. p., m. p. of fatty acids, and the reciprocal of the I no. They are 4166 for cacao butter and 5615 for illipe butter. A table of corrections for the "short factors" is also given. The consts. found for cacao butter were  $d_{15.5}^{20}$  0.8825;  $d_{15.5}^{25}$  0.8575, viscosity 99.9, m. p. 30.5, I no. 39.8, m. p. of fatty acids 48.4,  $n_D^{40}$  1.4569. The consts. for illipe butter were  $d_{15.5}^{20}$  0.8826,  $d_{15.5}^{25}$  0.8577, viscosity 103.7, m. p. 33.2, I no. 31.5, m. p. of fatty acids 52.8,  $n_D^{40}$  1.4568. The m. p. were detd. by placing a shaving of the fat on Hg in a crucible and heating gently. The m. p. was taken as the first appearance of transparency in the shaving. N. V. S. M.

**The uses of glycerol and its substitutes.** C. DEITE. *Z. deut. Oel-Fett-Ind.* **41**, 273-6, 290-3, 307-8, 321-3, 337-8, 355-6, 388-9(1921).—An enumeration of the uses of glycerol in pharmacy, cosmetics and soaps, the paper and textile industry, as printing ink and rolls, hectographs, explosives and in miscellaneous applications, with numerous formulas, derived from the technical and patent literature. Glycerol substitutes are discussed, among others glycol, KCl and  $\text{MgCl}_2$ , sugar solns., "Mollphorus," erythritol, Na lactate, trimethylglyccoll, etc. P. ESCHER

**Tasks of the fat-chemistry group of the Verein Deutscher Chemiker.** W. FAHRION. *Chem. Umschau* **28**, 137-8(1921).—A suggestion to the chemists of the Verein Deutscher Chem. to standardize fat-analytical methods, beginning with the I no. P. ESCHER

**Contribution to the study of the oil palm.** P. THON. *Belg. Min. Colon., Revent* **9**, 37-69(1920); *Expt. Sta. Record* **44**, 147.—A study of different varieties of the oil



palm (*Elais guineensis*) with reference to their yield in nuts and oil, including a comparative study of methods of extg. palm oil. The enemies of *Elais* are also briefly discussed.

H. G.

**Oil-seed plants.** H. WACKER. *Landw. Hefte* 1917, No. 32-3; pp. 66; *Expt. Sta. Record* 43, 638.—A treatise on the production of fats and oils from oil-seed plants, with statistics on the importation and extent of culture of the plants in Germany. Brief descriptions of rape, turnip, false flax, white and black mustard, radish, poppy, sunflower, flax, and hemp are included, together with lists of varieties, cultural methods, and comparative analyses.

H. G.

**New oil seeds.** K. STOECKERT. *Oel und Fettind.* 1920, 61; *Giorn. chim. ind. applicata* 2, 402-3(1920).—S. devised the following simple method for analysis of oil in seeds: Crush up a weighed amt. of seeds between 2 dried and weighed filter papers, with a hammer. The papers absorb the oil. They are then dried and weighed, and their increase in wt. gives the oil content with sufficient approximation. S. obtained the following results. The seeds of *Agrostemma githago* gave 5.32% oil. *Viola tricolor* gave 16.28% of a light yellow, limpid, non-drying oil. *Plantago major dolce* gave 22.08% of a lemon yellow to pale green oil, of agreeable sweet odor, the oil appearing to be edible. *Bursa pastoris* gave 17.4% of an intense yellow oil. *Galeopsis* gave 35.6% of a yellowish oil. *Ranunculus acris* gave 23% of an orange yellow drying oil, apparently suitable for varnishes. *Mellilotus officinalis* gave 8.35% of a greenish oil, having an odor similar to that of coumarin and is probably utilizable for pomades and cosmetics.

ROBERT S. POSMONTIER

**Composition of the oil and meal from seeds of sweet pepper.** E. COMANDUCCI AND A. TOMASINI. *Rend. accad. sci. Napoli* 27, 38-40(1921).—Extn. with Et<sub>2</sub>O of the dried and powdered seeds of sweet pepper (*Capsicum annuum*) gave 25.7% of fatty oil having a pungent odor and pungent sweetish taste, with a yellow color and greenish reflection.  $D_{20}^D$  0.9216,  $n_D^{20}$  1.4735, solidifying point 12°, acid no. 11.28, sapon. no. 184.6, ester no. 173.32, Reichert-Meisler no. 17.3, Ac value 39.96, relative I no. 129, absolute I no. 141.3, solid fatty acids 32%, liquid fatty acids 68%, m. p. of solid acids 40-43°, Behner no. 85.44, hydroxy acids 1.64%, glycerol 7.69%, unsaponifiable 2.74%, cholesterol 2.13%, Maumenee no. 89°, insol. in EtOH. The usual color reactions gave red-brown shades. Proper refining should yield an edible oil. The residue after extn. of the oil contained moisture at 105°, 9.46%, crude protein from total Kjeldahl N 21.35%, pure protein 3.238%, reducing sugars 0.74%, sucrose 0.55%, dextrin 0.98%, albuminoids affected by gastric digestion 14.49%, crude fiber 34.98%, ash 4.8%, P<sub>2</sub>O<sub>5</sub> 0.39%. The material is suitable for stock food.

M. R. SCHMIDT

**The sterilization of oils by means of ultra-violet rays.** LAWRENCE T. FAIRHALL AND PAUL M. BATES. *J. Bact.* 5, 49 (66-1920).—Certain oils, such as olive, cottonseed and almond, can be sterilized by a relatively short exposure to ultra-violet rays. The abiotic power of ultra-violet rays is not restricted to the vegetative bacterial cell, but extends to bacterial spores and to certain molds, such as *Penicillium*, *Aspergillus* and *Mucor*. The action of lipolytic enzymes in oil is inhibited by exposure to ultra-violet rays. The oil is unchanged except for a slight bleaching, but if olive oil is exposed for a long period of time, there is an increase in acidity which is proportional to the time. The sterilizing effect is still apparent after the rays have filtered through 4 mm. of oil.

JOHN T. MYERS

**Action of phosgene on ricinolein.** A. PIUTTI AND A. CURZIO. *Rend. accad. sci. Napoli* 27, 40-7(1921).—By passing COCl<sub>2</sub> through castor oil cooled with ice and NaCl, and heating the product in an autoclave for 1 hr. at 100°, or preferably by passing COCl<sub>2</sub> through the oil heated to 100°, and removing the excess of COCl<sub>2</sub> by repeated washing with H<sub>2</sub>O, and then drying *in vacuo* over H<sub>2</sub>SO<sub>4</sub>, a somewhat darker oil is



obtained,  $d > 1$ , insol. in EtOH, and consisting of almost pure *triglyceride of ricinolein chlorocarbonate*,  $C_{18}H_{33}(CO_2ClC_{17}H_{33}CO_2)_3$ . Cl was detd. by heating 0.2–0.5 g. of sample with  $Na_2CO_3$  in a deep Pt crucible, and titrating by Volhard's method; Cl found 8.90–9.15%, calcd. 9.51%. The average figure of 9% is taken as the *Cl index of castor oil*. Similarly, from ricinoleic acid, *ricinoleic acid monochlorocarbonate* was prepd., Cl found 9.55%, calcd. 9.84%. Olive, peanut, almond and sesame oils gave Cl indices of 0.08–0.18%. Mixts. of these oils in varying proportions with castor oil gave Cl indices corresponding very closely to the calcd. values, thus affording a means for *detecting adulteration of castor oil*. Also in *Giorn. chim. ind. applicata* 3, 242–4 (1921). M. R. SCHMIDT

A note on the oil of oats. ERNEST PAUL. *Analyst* 46, 238–9 (1921).—Oats were extd. with petroleum ether under pressure, and the ext. was freed from lecithin. The oil was a clear, yellow-green liquid at ordinary temps. It became thick and granular at 10° and solidified completely in 24 hrs. at 5°. It had an acid and biting taste. The properties were: m. approx. 8°,  $d_{4}^{25}$  0.925, acid no. 68.90, free fatty acid 34.70%, neutral fat 64%, sapon. no. 189.8, I no. (Wijs) 114.2, unsapon. 1.30%,  $n_D^{20}$  1.4701, insol. fatty acids 93.6%, acid no. of fatty acids 284.8, mean mol. wt. of fatty acids 234.8, I no. of fatty acids (Wijs) 127.1, m. p. of fatty acids 27.5°,  $n_D^{20}$  1.4635. These properties are compared with values given by Stellwaag (*Landw. Versuchs. Sta.* 37, 135–155). The oil only commences gumming in two months at ordinary temps. but forms a hard varnish at 99° in 2 to 3 days. NICHOLAS V. S. MUMFORD

Soap-washing process with reference to soap-saving. E. O. RASSER. *Seifen-sieder-Zig.* 48, 268–9, 290–1, 309–10, 355–7 (1921).—Ten German degrees of hardness (1° = 1 g. CaO per 100,000 g.) destroy 166 g. of soap per m<sup>2</sup>. and with soap at 0.80 Mk per kg. the loss per 100 l. H<sub>2</sub>O of 20° hardness amounts to 0.25 Mk or 25% of its cost. Much of the Ca and Mg soap accumulate in the washed goods as shown by their ash content: new shirts contain 0.5 to 3.0% ash, old shirts 7.3 to 8.8%, flannels 14%, mostly Ca and Mg with a little SiO<sub>2</sub>. Practical men consider that 1–2% soap solids produce a good lather while Krafft's expts. show that soaps of the individual fatty acids lather well at a concn. of 0.25 to 1.0% and Shukov and Shestokov found that commercial soaps give best effects at 0.2 to 0.6%. Margosches considers a soap to be bad when it requires boiling instead of lukewarm H<sub>2</sub>O to dissolve to a clear soln. Addition of rosin increases soly. and K soaps dissolve better than Na soaps and those of the liquid fatty acids easier than those of the solid acids; the milling of soaps and addition of silicate increases soly. and lathering power; glycerol soaps produce little foam. A review of the literature of the cleansing action of soaps (W. Fahrion, F. Goldschmidt, W. Spring, Margosches) is discussed, concluding with the statement that the ions of the H<sub>2</sub>O hydrolyze the soap, setting free weak fatty acids and strong alkali, which explains the alkaline reaction, while the acids recombine with undecomposed soap to form acid soaps that produce a lather with H<sub>2</sub>O and the free alkali recombines with undecomposed soap to form a basic soap. Much H<sub>2</sub>O increases hydrolysis so that the NaOH concn. is but little changed by the extra H<sub>2</sub>O. These solns. are colloidal solns. with a strongly increased surface contg. several phases in which the acid and basic soaps are the dispersed phase. This view is confirmed when such a soln. is electrolyzed, the acid soap going to the anode, the basic soap remaining in soln., while soot in an alkaline medium travels to the cathode, so that the negative acid soaps adsorb the positively charged soot, ferric acid or clay particles, etc., after the latter have been loosened from the fiber. Cellulose absorbs the particles of alk. soaps but not those of acid soaps. Thus the cleansing effect is an adsorption phenomenon of irreversible adsorption compds., the latter having lost their adsorption power after being once formed. Soap solns. decrease the surface tension and increase viscosity. E. Baur states that adsorption must always occur when increased concn. of particles in a surface decreases surface tension but a quant. relation



between adsorption and lowered surface tension could not be established by Patrick nor by Lewis. Normal soap solns. show no rise in b. p. and may, therefore, be considered true simple colloidal solns., the rise in b. p. of dil. solns. being due to free NaOH according to Krafft, but conductivity detns. by McBain and Taylor show that normal soaps even in concd. soln. are mixts. of colloidal acid soaps and free alkali. According to Botassi and Victorow concd. solns. are true colloidal solns. which on removal of some of their alkali become more or less coarse-grained suspensions of fatty acids and acid soaps. According to Buchner different soaps show the following order in cleansing power: tallow soaps, soaps from liquid vegetable oils or olein, coconut and palm-kernel oil soaps and rosin soaps. The greatest cleansing efficiency is obtained with 0.2 to 0.4% soap solns. The lathering ability and its cause are discussed and the work of Stiepel, Shorter, Margosches, Sommerhof, Reychler and Buchner is referred to and Buchner's theory of the cleansing action of soaps is cited.

P. ESCHER

**Scheme for determining the washing and cleansing effect of washing compounds.** P. HERRMANN. Staatl. Mat. Prüf. Amt. Berlin-Dahlem. *Z. deut. Oel-Fett-Ind.* 41, 338-41 (1921); *Textilber.* 2, 37-8, 61-2 (1921).—For the purpose of arriving at some standard method of testing the cleansing effect of washing compds., H. describes in detail a lab. method, which he gradually developed in the course of his investigations and discusses it under the following captions: (1) Washing and bleaching compds. These should be tested separately from each other. (2) Artificial and natural soiling. Artificial soiling is preferred as being under control for uniformity. (3) Expressing the cleansing effect. Expression in figures is recommended. (4) Basic substance for soiling the goods. The indigo-colloid of the Höchst. Farbwerke has been adopted on the recommendation of Dr. König of the Höchst works, as possessing uniform grain and being chemically inert. (5) Secondary substance for soiling. A gasoline soln. of machine oil is recommended and also a soln. of sizing material such as starch. (6) Comparison of different washing-tests series. Complete series, made with a large supply of cloths that have been soiled under the standard conditions, are suggested. (7) Standards for comparison. (a)  $\text{H}_2\text{O}$ , (b)  $\text{Na}_2\text{CO}_3$ , (c) soap powder of the War-Commission and (d) soap-soda are chosen as standards for comparison. (8) Working conditions of expts. Certain details of the methods are discussed (see No. 10), using  $50^\circ$  as standard temp. (9) Evaluation. Comparison by the eye is preferred and the judging by loss of wt. is rejected. (10) Summary. Air-dry, absorbent strips of wool, cotton or linen, free from starch, are soaked in a 0.5% indigo-paste soln. and pressed out until the goods weigh double their dry wt., after drying they are soaked in a 5% soln. of mineral oil in gasoline, allowed to drain and then shaken out by hand. 10 g. of the dried goods are washed (a) in 250 cc. distd.  $\text{H}_2\text{O}$ ; (b) in 250 cc. 0.5%  $\text{Na}_2\text{CO}_3$  soln.; (c) in 250 cc. 0.5% War-Com. soap powder; and (d) in 250 cc. soap-soda soln., contg. 1.25 g. of a 60% grained soap plus 0.75 g. anhydrous  $\text{Na}_2\text{CO}_3$  per l. distd.  $\text{H}_2\text{O}$ . The washing is done in porcelain dishes by strongly squeezing the goods by hand 20 times in the solns. at room temp., then heating to  $50^\circ$  for 15 min. with constant stirring, pressing them again 20 times; they are removed from the bath, again pressed 20 times each after 30, 45 and 60 min., a total of 100 pressings in 1 hr. They are rinsed in 40 to  $50^\circ$  distd.  $\text{H}_2\text{O}$  until no color is observed in the rinsing water and are finally ironed. The first washing-test with distd.  $\text{H}_2\text{O}$  represents zero while the soap-soda test represents 100. Two illustrations showing typical results accompany the article.

P. ESCHER

**Hardened oils in the soap industry.** M. O. STEFFAN. *Seifensieder-Ztg.* 48, 563-5 (1921).—Hardened oils when first used in soaps gave products which were too hard and deficient in lathering properties because too great a percentage was used. Practice has shown that 50% of  $40^\circ$  titer hard fat can be used without disadvantage and up to 70% in the case of a rosin soap of high rosin content. If the hardened oil



has a titer of 60 to 70°, it can be used in a rosin soap of 130% rosin content to the extent of 60% of the fat. The sapon. of the hardened oil is best made with weak lye; and the higher the degree of hydrogenation the less salt is required for graining the soap. Hardened oils are readily split by any of the processes used for this purpose. E. S.

**The ash of calcium-containing soaps.** E. LANTOS. *Chem. Ztg.* **44**, 35(1920); *Expt. Sta. Record* **43**, 412.—Attention is called to the fact that if org. substances contg. Ca are ashed to whiteness in the usual way the Ca is left in the form of the carbonate instead of the oxide. To overcome this, L. recommends adding a small amt. of  $\text{NH}_4\text{NO}_3$  to the substance and heating before the blast lamp. The ashing is said to require a much shorter time and to convert completely the Ca into the oxide. H. G.

The biochemistry of tobacco. II. Tobacco seeds (PARIS) 11D. Olive investigations (CRUESS, ZION) 12. Gossypol in cottonseed meal (WITHERS) 12.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Report of committee on agricultural progress of the Louisiana Sugar Planters' Association for the year 1920.** C. B. GOUAUX, J. M. CAFFERY AND ELLIOT JONES. *Louisiana Planter* **66**, 185-9(1921).—This report covers the work done on the planting and fertilizing of cane. A detailed report is given of the work done to eradicate the mosaic disease. C. H. CHRISTMAN

**The sugar industry in the Dutch colonial possessions.** J. BARKLEY PERCIVAL. *Louisiana Planter* **66**, 238(1921).—Sugar production in Java reaches as high as 15,000 lbs. per acre. The av. yield in 1917 was 10,117. Total production in 1919 was 1,319,809 tons. The sugar is sold as plantation whites, channel assortment polarizing 98°C or higher and 96 test sugar for refining. Ordinarily the Javanese supply is absorbed by the contiguous territory. C. H. CHRISTMAN

**Heat losses in sugar factories.** I. J. LASALLE. *Sugar* **23**, 200-1(1921).—Greatest losses of heat in sugar houses arise from inefficient burning of the bagasse, improper use of fuel oil in connection with the bagasse, and lack of insulation on steam and hot-water pipes. Unbalanced equipment also is a prominent factor in causing losses. Suggestions covering these points are offered. C. H. CHRISTMAN

**Equipment of modern beet sugar factories.** II CLAASSEN. *Z. Ver. deut. Ing.* **65**, 545-8, 571-3(1921).—A condensed description is given of the various machines and other technical devices used at present in Germany for the transportation, unloading, washing and slicing of beets; for the extn. of the juice by diffusion, by the Steffen lixiviation-diffusion process, by the Claassen method with return of waste waters, and by the Hyross press-diffusion process; for the clarification of juices and sirups, for the evapn. of sirup to grain; and for the recovery of by-products and the treatment of the effluent. Illustrated. F. W. ZERBAN

**Sugar and alcohol from the agave or century plant.** E. DELAFOND. *Louisiana Planter* **66**, 395(1921).—An electrical treatment of the juice of the agave removes impurities which have hitherto prevented the crystn. of sugar from this source. The treated juice can also be fermented while the non-treated juice is not fermentable. C. H. CHRISTMAN

**Glucose and starch from maize.** T. D. HALL AND G. M. HAY. *S. African J. Ind.* **3**, 597-605(1920); *Expt. Sta. Record* **44**, 434.—Brazilian Flour, Hickory King, and Chester County corn were included in this exptl. study, which reports the detn. of starch and glucose yields, sol. reducing carbohydrates in corn meal, nature of sol.



carbohydrates, oil content and I values, and other analytical data. The authors are inclined to think "that Hickory King and Chester County are better than Brazilian Flour corn for the manuf. of starch and glucose in South Africa, as at present they are so much more easily procurable in quantity, yield almost as much glucose, and have a smaller loss in grinding. Both Hickory King and Chester County are more easily grown on the av. soil, and yield more heavily than Brazilian Four corn." H. G.

**The Kestner process.** P. KESTNER. *J. fabr. sucre* 61, No. 12, 1(1920); *Expt. Sta. Record* 44, 414.—In this article K. emphasizes the point that the process described (cf. C. A. 14, 2101) is in no sense designed to compete with the present sugar industry, but should be of considerable interest in places where small factories could be installed to take care of the local sugar-beet production. H. G.

**The composition of the carboraffin used in the filtration of refinery clearers and of the sweet waters resulting therefrom.** Vt. ŠKOLA. *Listy Cukrovár.* 39, 293-8(1921).—Continuing the researches on the decolorizing carbon, "carboraffin," (C. A. 13, 1544, 2613; 15, 772) Š. studied the removal of various adsorbed substances from the used carboraffin during the sweetening-off operation. First, 2nd and 3rd clearers were passed in sequence through the filter presses filled with carboraffin. 0.03-0.06 g. of CaO per 100 g. of liquor were added to the first clearer and, after bringing to a boil, the alkalinity was reduced to a lime content of 0.002-0.006 g. per 100 g. of liquor by sulfitation. After a preliminary mechanical filtration, the juice was passed through the carboraffin. The 2nd and 3rd clearers were prepd. by dilg. the corresponding sirups resulting during the production of white sugar and were similarly treated with lime and  $\text{SO}_2$ . During the filtration of the juices, CaO was retained to a very great extent. The remaining ash constituents of the juices were adsorbed in lesser amts. ZnO was leached out continuously from the carboraffin by the juices. Alkalies were removed completely from the carboraffin by the sweetening-off operation. 96.7% of the adsorbed CaO was retained. Nevertheless, the resulting sweet water was richest in CaO, which pptd. out as  $\text{CaSO}_4$  during concn. Zn also was present. Of the alkalies,  $\text{K}_2\text{O}$  and the chlorides leached out in large quantities at the start. At the end of the operation  $\text{Na}_2\text{O}$  and the sulfates were predominating. During the filtration a filter press containing 234 kg. of dry carboraffin retained 47.44 kg. of ash. The sweetening process removed the following:  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  0.18 kg., CaO 1.31 kg., MgO 0.17 kg., ZnO 0.19 kg., alkalies 1.17 kg. This is equal to 6.4% of the total adsorbed ash. JOHN M. KRNO

**Quantity of lime for defecation.** ARNOLD H. WARREN. *Sugar* 23, 357-8(1921).—Owing to wide fluctuations of acidity in juices and to varying strengths of lime used for defecation, W. proposes a system of adding a predetd. quantity of milk of lime sufficient to bring the acidity to 0.3. Milk of lime is made up to 20° Bè and 10 cc. is titrated against N HCl. The CaO content as g. of CaO per l. of milk of lime is found by multiplying cc. HCl used by 2.8. The % acidity of the juice is obtained by titrating 10 cc. juice with 0.1 N NaOH. 
$$\frac{28.035 \times 1.4}{11} \times 0.3 = \%$$
 milk of lime by vol. required to bring

1000 gal. mixed juice to 0.3 acidity; 1 = acidity of juice and W = g. of CaO per l. in the milk of lime. The method of prepg. milk of lime and the app. used in making the addition to juice are outlined. C. H. CHRISTMAN

**The relation between the sugar content of the pulp and of the press water in the diffusion battery of the beet sugar factory.** A. L. VAN SCHERPENBERG. *Chem. Weekblad* 18, 328-35(1921).—The purpose of this investigation was to find a way for reducing the necessary large number of analyses of pulp and press water to a minimum. As long as the working conditions in the factory are the same, there must be a functional relationship between the sugar contents of the two materials, so that the analysis of one should be sufficient, the other being calcd. V. has established this functional relation



by the application of statistical methods. A table is first constructed, on which the sugar content of the press water is plotted horizontally, in steps of 0.01%, and that of the pulp vertically, in steps of 0.05%. Then the number of analyses, covering an entire campaign, in which a certain % sugar in the press water corresponds to a certain % sugar in the pulp, are filled in for each graduated step at the intersection of the lines and columns. From these figures the mean values for the sugar contents of water and pulp ( $M_1$  and  $M_2$ ), and the standard deviations from these means ( $b_1$  and  $b_2$ ), as well as the correlation coefficient  $r$  can be calcd. If  $x$  be the sugar content of the press water, and  $y$  that of the pulp, then  $y = r \times [b_1/b_2] \times (x - M_1) + M_2$ , and  $x = r \times [b_2/b_1] \times (y - M_2) + M_1$ . (For details of the calcs. the works on the theory of statistics should be consulted.) At the factory in question, it was found that for three successive campaigns,  $y = 2.47x - 0.278$ . If factory methods are changed, the function must be redetd., but otherwise it is necessary only to analyze the press water regularly; as a safety measure the pulp should be analyzed once every 4 hrs.

F. W. ZERBAN

**The recovery of ammonia in beet sugar manufacture.** K. ANDRLÍK AND V. ŠKOLA. *Listy Cukrovar.* 39, 149-152, 157-9, 161-4(1921); *Z. Zuckerind. Echo Slov. Rep.* 45, 179-82, 187-90, 195-8(1921).—From the analysis of the juices it was found that the amt. of  $\text{NH}_3$  liberated, calcd. on the wt. of roots sliced, was 0.0019% (12.5% of the total) during carbonatation. The amt. of  $\text{NH}_3$  recovered from the gases escaping during satn. reached a total of 0.00075% for both satns., which is 40% of the total present. During the heating after the satn. was completed, 0.0058%  $\text{NH}_3$  (38.4% of the total) was lost. The condensed waters coming from the quadruple-effect evaporators contained 0.0074% (49.0% of the total). A small amt. was lost during filtration in the filter presses. The above results show that in considering the technical recovery of ammonia, that lost during evapn. and in the condensed waters is of prime importance. The recovery of the latter has not been accomplished economically. Recovery by distn. as will be shown later is too expensive.

JOHN M. KRNO

**Sucrose in seed beets.** SYDNEY F. SHERRWOOD. *Sugar* 23, 299-300(1921).—The Keil boring rasp and the Clark press for sampling sugar beets are not satisfactory because of the losses caused in sampling. A suitable device consists of an ordinary  $1/16$  wood boring bit operated by a  $1/2$  h. p. motor at 1750 r. p. m. This produces hole in the beet into which a specially designed rasp is run. The pulp obtained is very fine and well suited for rapid extrn. Thirteen g. of pulp and 88.5 cc. of a soln. of 100 cc. lead subacetate sp. gr. 1.25 to each gallon of water are placed in a cup, the cover is placed on the cup and allowed to stand 15 min. After filtering a drop of glacial acetic acid is added and the soln. polarized in a 200- or 400-mm. continuous tube. The results compare very favorably with those of Pellet's hot water method. C. H. C.

**Simplified sucrose determinations.** CHARLES R. GERTH. *Sugar* 23, 369(1921).—For sugars or thin juices G. polarizes and inverts according to the method of Walker. Sucrose = [Direct Reading—2(Invert Reading)]/[Constant—0.5 Temp.]. For sirups, molasses and Steffen-house products, 35.75 g. of sample are dissolved in water, clarified with lead acetate, made up to 250 cc. and filtered. Fifty cc. of filtrate and 1 cc. satd.  $\text{Al}_2(\text{SO}_4)_3$  soln. are made up to 55 cc., filtered and polarized at 20° in a 2-dm. tube. Reading  $\times 2$  = Direct Polarization. Seventy-five cc. of filtrate are inverted, cooled, made up to 100 cc. and filtered. A small amt. of zinc dust is used for clarification and after filtration the soln. is polarized in a 2-dm. tube. Sucrose = [Direct Reading—(8/3 Invert  $\times 10/11$ )]/[Constant—0.5 Temperature]. A table of const. is given. These correspond to various polariscopic readings after inversion and to different temps.

C. H. CHRISTMAN

**The mottling or yellow stripe disease of sugar cane.** J. A. STEVENSON. *J. Dept. Agr. and Labor Porto Rico* 3, No. 3, 3-78(1919); *Expt. Sta. Record* 42, 744.—



Earlier reports (*Porto Rico Dept. Agr. Sta. Rept. 1917*, 40-78; *Rev. Agr. Puerto Rico* **I**, No. 1-2, 18-25(1918)) regarding the disease of sugar cane which has been raging in Porto Rico unchecked for several years are followed up with a systematic account of studies on this trouble, for which the descriptive name mottling disease is preferred. No direct relation has been established between the disease and nature of soils, years in cane, methods of prep. the laod, drainage, or other cultural features. No direct influence was demonstrated in case of fertilizers, liming, seed treatment, manner of disposing of trash, or moisture content of the soil. An accumulative effect in successive ratoon crops is apparent. The disease has not been transmitted artificially. Chem. tests of the juice do not show any abnormal glucose ration or any const. difference between the juice of oormal and that of diseased canes. H. C.

**Cane milling and juice clarifying.** CLEVE W. HINES. *Sugar* 23, 329-31(1921).—The amt. of trash in cane should be ascertained in order to base yields upon clean cane. Clarification through the use of lime and S, lime and phosphoric acid and salts, lime and carbonic acid, hyposulfite, bluing and bone charcoal is described. C. H. C.

**An innovation in the manner of liming cane juices.** M. BIRD. *Louisiana Planter* 66, 185(1921).—To avoid losses in sucrose between the mills and liming tanks B. introduced lime and formaldehyde into the juice of the last mill. This juice was used as maceration water and rendered all the mill juice neutral. Better clarification, smaller fluctuations in acidity, and lower losses of sucrose were thus obtained. C. H. C.

**Operating the sugar factory lime kiln.** ANON. *Sugar* 23, 137(1921).—Uneven distribution of coarse and fine limestone and the coke often produce under burning. Proper burning follows when the kiln is only partially filled with limestone and coke until the proper rate of burning is obtained. The addition of limestone with 12% coke at the proper rate gives satisfactory burning of the limestone and also the necessary gas for carbonations. C. H. CHRISTMAN

**Hydraulic centrifugals.** BRENO C. LECHLER. *Louisiana Planter* 67, 29-31(1921).

The principles underlying the use of hydraulic centrifugals are described. The shapes of buckets and the factors governing these shapes are presented. Practical limitations are: principally from variability in the hydraulic pressure and details of construction. With a head of 350 feet available, hydraulic centrifugals would prove ideal. C. H. C.

**"Sugola" a new type of sirup.** C. S. HUDSON. *Am. Food J.* 16, No. 4, 11-13(1921).—The Brown-Duryea process for mfg. a sirup from starchy foods (corn, flour, etc., cassava, etc.) containing maltose 70-76, dextrose 2-6, dextrin 1-4, H<sub>2</sub>O 20-22, 0.3-0.4 and nitrogenous substances 0.3-0.8% with pure sweet flavor free from malt, used on the patent of Duryea (C. A. 8, 3637) is described with drawings of the plant. H. A. LEPPER

**Palm gur manufacture in the Bombay Presidency.** V. G. GOKHALE. *Dept. Agr. Bombay Bull.* 93, pp. 11-66(1919); *Expt. Sta. Record* 43, 808.—This consists of a brief historical account of attempts at gur making from date palms, the report of a series of investigations conducted from 1915-19 on the possibilities of the com. manufacture of palm gur, a detailed description of the process of tapping the juice and making gur, and appendices by P. C. Patil on gur making from brab, coconut, and *Bherli* palms, including data on the quantity per tree, chem. compn., deterioration on keeping, and effect of different preservatives of the juice and gur of palms. H. C.

**Gur making from the juice of the date palm (*Phoenix sylvestis*) in the Thama district of the Bombay Presidency.** V. G. PATWARDHAN. *Louisiana Planter* 66, 190-1(1921).—See C. A. 15, 956. C. H. CHRISTMAN

**Starch, starch granules, and starch solutions.** W. BIEDERMANN. *Arch. ges. Physiol.* 183, 168-96(1920).—Natural starch consists of a mixt. of two entirely individual substances, amylose (which is identical with granulose or  $\beta$ -amylose) and amylo-



pectin. The amylose when mixed with I gives a blue color; amylopectin mixed with I yields a violet color. Amylose does not form a paste; amylopectin when heated with water gelatinizes. In hot water amylose does not give a true soln., the product is rather a hydrogel. In treating starch with water the temp. of extrn. is important with regard to the yield of amylose; the greater portion is extrd. at 80 degrees. Somewhat more can be obtained by extrn. at 90 degrees, but for complete removal the boiling temp. is necessary. The stromata of the starch can be rendered achromatic by the activity of saliva. Such digested stromata do not stain with I. This stromata represents the "skeleton" of the starch granule and is amylocellulose, which may be present in admixture with amylopectin or as individual particles. The microscopic characteristics of starch under various types of treatment are shown, and the nature of the starches derived from different sources is discussed. G. H. S.

Technic of potato starch manufacture. C. C. MOORE. *Potato Mag.* 2, No. 12, 10, 11, 20, 22, 23; 3, No. 1, 8, 9, 20, 22, 23 (1920); *Expt. Sta. Record* 43, 808.—This paper consists of a detailed description of the various processes in the manuf. of potato starch, together with a discussion of the marketing possibilities of the product. H. G.

Polarimetric estimation of starch. H. LÜHRIG. *Pharm. Zentralhalle* 62, 141-4 (1921).—Ewer's method (*C. A.* 2, 1844, 2881) gives the most consistent results and is not appreciably influenced by variations in the concn. of the acid used. The time of heating, 15 min., must not be varied, and if continued over 16 min. low results are obtained. The method of Mauwich and Lenz (*C. A.* 14, 3481) in which the starch is dissolved in a  $\text{CaCl}_2$  soln. acidified with  $\text{AcOH}$  and boiled 15 min. gives consistent results. H. A. SHONLE

Lime kilns and lime burning (MEADE) 20. Production of industrial alcohol on sugar estates (DEMING) 16. Paper from bagasse (ANON) 23. How to convert sugarcane megass into a profitable fertilizer (RAO) 15.

Apparatus for preparing dextrin. WATARU KUMAGAI. Japan 36,697, July 1, 1920. A water-cooled spiral conveyer is provided in the bottom of the heating chamber. 100 lbs. starch are mixed with 8 lbs.  $\text{HNO}_3$  of 38° Bé and dried. The mixt. is introduced into the chamber heated at 300° F. and agitated for 2 or 4 hrs. By short heating white dextrin is produced, while by longer heating a yellowish white gummy product is formed. The product is obtained in powder and does not contain glucose.

## 29 - LEATHER AND GLUE

ALLEN ROGERS

An "insoluble" hide powder. H. R. ZEUTHEN. *Collegium* 1921, 181-2.—Chromed hide powder was washed with water in the usual way and then dried by washing repeatedly with alc. Results of analyses with this and with freshly washed hide powder made every few months during the year all showed good agreement. The hide powder should not be ground until after it has been chromed and washed or (1) washing on a large scale will be very difficult and (2) the powder will not wet up properly owing to the fact that the surface of the particles is strongly chrome tanned. Also in *J. Soc. Leather Trades' Chem.* 5, 175 7 (1921). I. D. CLARKE

The ability of hide powder to adsorb acid in the presence of formaldehyde, with special consideration of acid dyes. O. GERNGROSS. *Collegium* 1921, 169-81.—Skin is, as Moeller states, hydrolyzed by acid (*C. A.* 15, 1638) so that in studying the adsorption of acid by skin it is necessary to use dil. acid and to allow it to act only for a



short time instead of for several months as Moeller does. Equil. is usually reached in less than an hour and in this time hydrolysis of a hide powder lightly tanned with HCHO is negligible. The HCHO treated hide powder used in these expts. had a water resistance, measured by Fahrion's method (*C. A.* 3, 2253), of 48 while the resistance of the untreated powder was 5.2. Direct comparisons were made of the treated, and the untreated hide powder and of water blanks. The HCHO treated powder adsorbed less acetic acid in every case than did the untreated. The least difference was 26% with a 0.2 *N* soln. and the greatest 46% with a 0.02 *N* soln. The adsorption of picric acid also was measured and the solns. were analyzed colorimetrically as well as by titration. The results agreed well so the lesser adsorption of acid by treated powder was not due to a faulty method of analysis. From 10% to 26% less acid was adsorbed by the treated hide powder as the concn. of the acid decreased from 0.07 *N* to 0.003 *N*. The adsorption followed the adsorption law to about 0.015 *N* and then quickly approached satn. at higher concn. The action of hide powder is, therefore, different from that of silk, wool or carbon. The decrease in adsorption caused by HCHO is not due as Moeller suggests, to a coating of HCHO on the fibers, for the adsorption of basic dyes is increased by HCHO. If an acid dye has been adsorbed by hide powder and HCHO is then added the dye will be partially set free.

I. D. CLARKE

Some scientific aspects of tanning. JOSEPH TURNEY WOOD. *Inst. of Chemistry of Great Britain and Ireland* 1920, 30 pp.—A lecture.

ALBERT R. MERZ

Vegetable tanning materials and their significance for our tanning industry. R. LAUFFMANN. *Z. angew. Chem.* 1921, Wirtschaft. Teil, 89-91; cf. *C. A.* 14, 233.—Before the war Germany imported 5/6 of her tanning materials, the balance being produced at home from oak and hemlock bark. The various vegetable tanning materials are described and discussed. The following table of av. percentage compn. is given:

Material.	H <sub>2</sub> O.	TANN.		NON-TANN.		Sugars
		Filter Method	Shaking M.	Filter M.	Shaking M.	
Oak Bark	13.0	10.0	9.0	5.5	6.5	2.6
Hemlock Bark	14.5	11.5	9.5	7.0	9.0	5.0
Mimosa Bark	14.5	33.0	31.5	9.0	10.5	4.0
Mangrove Bark	14.5	36.0	34.5	9.0	10.5	0.8
Wattle Bark	14.5	42.0	38.0	7.0	11.0	2.5
Nalanea	14.5	29.0	27.0	12.0	14.0	6.0
Myrobalans	13.0	31.0	30.0	14.0	18.0	5.5
Myrobalans with- out kernel	13.0	50.0	45.0	17.5	22.5	8.0
Dividivi	13.5	41.5	36.5	19.5	24.5	10.0
Nut Galls	16.5	30.0	27.5	7.5	10.0	....
Quebracho	14.5	20.0	19.0	1.5	2.5	0.3
Sumach	12.0	25.0	23.0	16.0	18.0	4.5
Tullo	11.5	40.0	37.0	13.5	16.5	3.5

JEROME ALEXANDER

Sole leather. CÉSAR SCHIAPARELLI. *J. Soc. Leather Trades' Chem.* 5, 44-56 (1921).—A study of Italian sole leathers used in military boots. Methods and results are given for the following "coefficients": hygroscopicity, firmness; soluble material; permeability; ash; ability to hold nails; deformation. Generally the more sol. matter a leather contains, the more permeable it is.

JEROME ALEXANDER

Further study of the guayacán (*Caesalpinia melanocarpa*). BARTOLOMÉ PÉREZ. *Informes dept. investigaciones indust. Univ. Tucuman* No. 6, 17-24 (1918).—A histological and chemical study of this tannin-bearing plant. Cf. *C. A.* 15, 1419. L. E. G.



Contribution to the knowledge of quebracho. LUDWIG JABLONSKI AND HANS EINBERG. *Collegium* 1921, 188-92.—Fluorescein is produced by fusing 1 part of quebracho ext. with 2 parts of phthalic anhydride and a little  $ZnCl_2$  and this can be used as a test for either pure or sulfited quebracho ext. If other tanning materials are present it is necessary first to ext. a water soln. of the material with  $EtOAc$  and use the residue from the evapn. of the  $EtOAc$  for the phthalic anhydride fusion. By this method 5% of quebracho can be detected in a mixed ext. For leather, ext. the fat-free leather with alc., dissolve the alc. ext. in water and treat the water soln. with  $EtOAc$  in the usual way. Tanned hide powder from analysis can be fused directly. Mimosa also gives the test and the differences between mimosa and quebracho have not yet been worked out. Resorcinol was found among the oxidation products of quebracho ext. and an attempt was made to isolate it from the unoxidized ext., but no indications of its presence could be found. Other substances were isolated but only fisetin could be identified.

I. D. CLARKE

The reactions taking place during the oxidation of unhaird skins. W. MOELLER. *Collegium* 1921, 161-9.—Amino acids are oxidized by  $H_2O_2$  with the production of  $CO_2$ ,  $NH_3$  and an acid and an aldehyde each with one C atom less per mol. than the original substance. The same reaction must take place during oxidation of the decompn. products of skin for these contain amino acids. The aldehyde has a slight tanning action but this does not proceed far owing to the hydrolysis of the skin by the acid.  $KMnO_4$  is a stronger oxidizing agent than  $H_2O_2$  but the action does not proceed as far owing to a deposit of  $MnO_2$ , which forms on the fibers. The collagen itself is not oxidized until after it has been hydrolyzed. Halogens probably do not oxidize collagen but do form insol. addition or oxidation products with the decompn. products. Cl and Br do not tan skins but I forms a colloidal soln. with the decompn. products and thus forms a true tanning system. The amino acids are oxidized by quinone and chromic acid in the same manner as by  $H_2O_2$ . If an analytical soln. has been treated with hide powder the decompn. products remaining in soln. will cause results by the iodometric method to be too high and results for formaldehyde by the peroxide method also to be too high.

I. D. CLARKE

Advances in the chemistry and industry of glue. RICHARD KISSLING. *Chem. Ztg.* 45, 629-32(1921).

E. H.

The testing of glue. ANON. *Farben-Ztg.* 26, 2477(1921).—A very brief outline of methods for detg. m. p., viscosity, mineral and org. acids, fat content, and foaming value of glues—factors which give indications of the amt. of foreign matter present.

F. A. WERTZ

The foaming of glue solutions. ANON. *Farben-Ztg.* 26, 2291(1921).—Glue solns. which tend to foam are objectionable because they are difficult to spread uniformly, and prevent max. adhesion because of the encased air bubbles. This property is influenced by a high peptone content and by certain org. impurities; and is usually due to the presence of free acids or alkalis, to the addition of Zn compds., too long heating of the glue stock, and the presence of mucin. The "foaming" value of a glue is best detd. by the method of Trotman and Hackford in which the sample is compared by a uniform procedure with a standard glue. Slow evapn. of the glue stock favors foaming probably on account of hydrolysis of gelatin into gelatone. To prevent foaming when making a liquid glue, the dry glue broken into small pieces should first be soaked in cold  $H_2O$ , and any foam, which forms after boiling, skimmed off. Addition of a small quantity of alc. or raw milk to the warm glue soln. reduces the tendency to foam.

F. A. W.



## 30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

**The history of synthetic rubber.** FRITZ HOFMANN. *Breslau. Z. angew. Chem.* 33, Aufsatzteil, 77-8(1920); cf. *C. A.* 6, 2331, 3025.—A continuation of the long controversy over the actual priority in the synthesis of rubber from isoprene. It is claimed that in 1909 Harries acknowledged its synthesis by H. at the Bayer Co. at Elberfeld. Later in his "Untersuehungen über die natürlichen und künstlichen Kautschukarten" he has laid claim to priority (*Ber.* 35, 3265(1902)). No mention is made of the work of Tilden.

C. C. DAVIS

**The Icken-Down process of preparing rubber.** O. DE VRIES AND W. SPOON. *Arch. Rubbercult.* 5, 204-22(1921).—The process does not, as has been claimed, increase the weight of rubber obtained from a given amt. of latex. Rubber prepd. by the process is similar to control samples in chem. compn. and vulcanizing properties; during a year's keeping it does not deteriorate.

G. S. WHITBY

**Pitch hydrocarbons used in the rubber industry.** FREDERIC DANNERTH. *India Rubber World* 64, 821-4(1921).—A summary of the properties of, and the principal tests applied to the hard hydrocarbons used in rubber manuf.

J. B. T.

**Vulcanization of rubber in sol and gel form.** HENRY P. STEVENS. *Rubber Age* 9, 295-297(1921).—Rubber in soln. may, by heating, be so vulcanized that a clear viscous soln. is obtained. The film resulting when the solvent is removed is indistinguishable from ordinary hot vulcanized rubber, and such films cannot be brought back to the condition of a clear soln. without decompn. of the rubber. When immersed in the ordinary solvents for rubber, such as benzene, the rubber films merely swell to form a gel.

J. B. T.

**Latex coagulated with a saccharated solution of lime.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 2, 144(1920).—The yield of crepe rubber obtained on coagulating latex with a soln. of lime and sugar (saccharated soln. of lime, B. P.) was 2% less than the normal; the rubber gave an acetone ext. of 3.4% and was of good quality, with a somewhat higher breaking strength and greater rate of vulcanization than the average.

J. S. C. I.

**Variation in fine hard para and plantation rubber.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 2, 347-50(1920).—An examn. of the rate of vulcanization of rubber from five loaves of wild para rubber revealed a variation comparable with that observed with properly prepd. smoked sheet plantation rubber (cf. Eaton, Grantham, and Day, *C. A.* 13, 1165).

J. S. C. I.

**Ageing of vulcanized plantation rubber.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 2, 270-6(1920).—Earlier observations (*C. A.* 13, 387, 675) have been extended by expts. with three mixts. of rubber 60, S 3, and ZnO 37 parts, the rubber consisting of plantation pale crepe, plantation smoked sheet, and fine hard para rubber, resp. When kept in a vulcanized condition for 3½ years the coeff. of vulcanization underwent a distinct increase, the extent of which (an av. of 0.27 for an initial coeff. of 2-3 and 0.40 for 3-4) was rather greater than that observed with the earlier mixt. of rubber 90% and S 10% at a comparable initial degree of vulcanization. Physical tests after an ageing period of 120 weeks showed that, if the initial coeff. did not exceed 3.5, the breaking strain first increased to a max. and then began to decrease, the highest final values being obtained for the samples with the lowest coeffs. The initial breaking strength and elongation of each of the mixts. contg. ZnO, unlike those of a simple rubber-S mixt., were very similar whatever the degree of vulcanization, the smoked sheet rubber giving the highest breaking strain and the lowest extensibility. The curves representing the



alteration of tensile strength and elongation with ageing tend towards a horizontal course after the breaking strength has fallen below 600 g. per sq. mm. For relative stability in vulcanized mixts. of this type it is found that the coeff. of vulcanization should not exceed a value of 2-2.5, this limit being lower than for a mixt. of 90% rubber with 10% of S.

J. S. C. I.

Recent work of Harries on caoutchouc. G. S. WHITBY. *India Rubber J.* 61, 313-5(1921).—An account of Harries' latest work on the constitution of the caoutchouc mol. and the nature of vulcanization, including some remarks on polymerization and on the form of large-scale extn. app. used by H.

G. S. W.

Odorless rubber. SHINJI SHIRAI, SADAKICHI TANAKA and BENNOSUKE YOSHIKAWA. Japan 36,754, July 16, 1920. Vulcanization is conducted with  $\text{Na}_2\text{CO}_3$  and soda ash instead of S. The product has the same elasticity as that of the usual product and is suitable for vessels contg. foodstuffs. The raw materials are rolled to a thin film, washed with  $\text{H}_2\text{O}$ , boiled with  $\text{H}_2\text{O}$  for 5 hrs., rolled with a hot roller to a colloidal state and mixed with an equal wt. of  $\text{Na}_2\text{CO}_3$  and half as much  $\text{CaO}$  at  $80-100^\circ$ , boiled with  $\text{NaOH}$  of  $30^\circ \text{Bé}$  for 5 hrs., treated with soda ash soln. of  $20^\circ \text{Bé}$  for 1 hr., and washed with  $\text{H}_2\text{O}$ .



















